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I THE α AND β ISOMERS OF
2,2'-DIPYRIDYLGLYOXIME

II ANALYTICAL APPLICATIONS OF
2,2'-DIPYRIDYL- α -GLYOXIME

BY

DONALD K. SOULES

A Dissertation
Submitted to the Faculty of Graduate Studies through the
Department of Chemistry in Partial Fulfillment of the
Requirements for the Degree of Doctor of
Philosophy at the University of Windsor

Windsor, Ontario
1971

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ABSTRACT

PART I

THE α AND β ISOMERS OF 2,2'-DIPYRIDYLGLYOXIME

The preparation, separation and characterization of the α and β isomers of 2,2'-dipyridylglyoxime are described. The α and β configurations are assigned on the basis of NMR, IR and chemical data.

PART II

ANALYTICAL APPLICATIONS OF 2,2'-DIPYRIDYL- α -GLYOXIME

2,2'-Dipyridyl- α -glyoxime has been found to be a highly selective reagent for the spectrophotometric determination of palladium, gold and iron (II). The determination of palladium and gold involve extraction into organic media. The effects of pH, solvents, time, heating, reagent concentration, buffers, ion-pairing, and diverse ions were studied. Beer's law was followed in all cases. The palladium chelate exhibited an absorption maximum at

404 nm, $\epsilon = 1.01 \times 10^4$, the absorption maximum for the gold complex in 4:1 dichloromethane-n-amyl alcohol solution was 448 nm, $\epsilon = 1.80 \times 10^4$, and the iron complex exhibited an absorption maximum at 534 nm, $\epsilon = 1.33 \times 10^4$.

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ANALYTICAL APPLICATIONS OF

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PART I

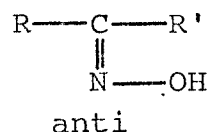
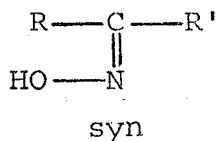
THE α AND β ISOMERS OF

2,2'-DIPYRIDYLGLYOXIME

CHAPTER I

INTRODUCTION

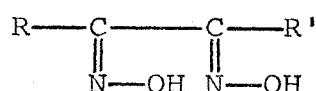
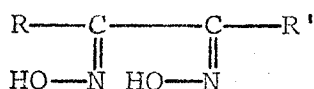
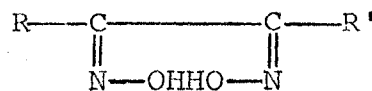
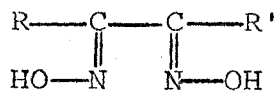
Oximes, that is compounds having a C=N-O-H grouping, exhibit some interesting stereochemical possibilities. The existence of the double bond with its restriction of rotation between the carbon and nitrogen atoms of the oxime group gives rise to the possible existence of two geometrical isomers of these compounds (1). These isomers can be labelled syn or anti depending upon the geometric configuration of the oxime group with respect to a reference group, R, of the compound in question (2, 3).



In the special case where R and R' are the same, the two isomers become one. This is the situation observed in symmetrical ketoximes.

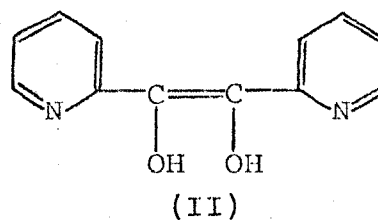
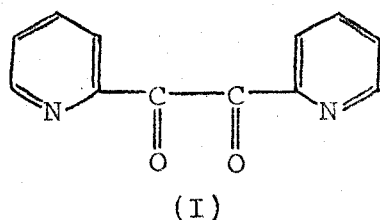
Vicinal dioximes, commonly known as glyoximes, can, by the nature of the two oxime groups in the molecule, exist in a maximum of four geometrical isomeric configurations (3). These forms have been labelled α , β , γ and δ dependent

upon the configuration of the oxime groups with reference to a specific group or groups within the molecule.



In the event that the groups R and R' are equivalent, the α and δ isomers become the same and a maximum of three isomeric forms, labelled α , β and γ , becomes possible.

In analytical applications it often becomes necessary to examine isomeric considerations in the use of some compounds as reagents. Excellent examples of this fact are shown in the cases of glyoximes. α -Glyoximes are well known as analytical chelating agents (4, 5, 6) whereas the β and γ forms are, in most cases, not usable as chelating agents. Thus, the isolation and characterization of the glyoximes derived from α -pyridil (I) and α -pyridoin (II) should prove fruitful for future consideration as analytical reagents.



In 1951, Mathes et al. (7) reported the isolation of a glyoxime, mp 215° , from the reaction of α -pyridil with hydroxylamine. In 1957, Trask (8) also reported the isolation of a glyoxime of α -pyridil, mp 215° , which was subsequently suggested as a reagent for the spectrophotometric determination of rhenium (VII) (9). In neither case was any attempt made at isomer separation and characterization. In 1961, Sadler and Pitman (10) reported the isolation of two glyoximes of α -pyridil, which melted at 235° and 247° . In a later communication (11), the α and β configurations respectively were assigned to the isomers on the basis of infrared spectral comparison with the α and β isomers of benzil dioxime. In 1969, the isolation of a glyoxime, mp $259 - 260^{\circ}$, from α -pyridoin and its application to the spectrophotometric determination of trace amounts of palladium (II) was reported (12).

In the present work, the isolation of two isomers of 2,2'-dipyridylglyoxime, mp $233 - 234^{\circ}$ and $264 - 265^{\circ}$, and assignment of configuration of isomers on the basis of both spectral and chemical data is given.

CHAPTER II

EXPERIMENTAL

A. MATERIALS AND APPARATUS

1) Apparatus

All Nuclear Magnetic Resonance spectra were obtained using 5% w/v solutions of the oximes in deuterated dimethylsulfoxide with TMS as the internal standard. These spectra were obtained with a JNM-C-60 HL spectrometer at room temperature (25°C).

Infrared spectra were obtained with a Beckman IR-12 infrared spectrometer using 1% w/w potassium bromide discs.

Ultraviolet spectra were obtained in ethanol with a Beckman Model DB spectrophotometer equipped with a Wavelength Drive Unit and a Sargent SRL recorder.

Uncorrected melting points were obtained with a Fisher-Johns Melting Point Apparatus.

2) Reagents

α -Pyridil and α -pyridoin were obtained from Aldrich Chemical Company and used without further purification.

Hydroxylamine hydrochloride, analytical reagent grade, was obtained from Mallinckrodt Chemical Works.

Pyridine, A.C.S. reagent grade, from Fisher Chemical Company was used after redistillation.

Ethanol, 95%, was used in all cases.

Dimethylsulfoxide, Fisher Certified grade, was used.

Deuterated dimethylsulfoxide, obtained from NMR Specialties, Inc., was used.

Nickel (II) chloride, sodium cyanide, ammonium hydroxide and hydrochloric acid were all A.C.S. reagent grade.

Distilled water was used in all cases.

B. SYNTHESSES AND SEPARATIONS

1) Synthesis of the Mixed Oximes

To a 500-ml round bottom flask, equipped with a reflux condenser, were added 30.0 g (0.14 mole) of α -pyridoin, 300 ml of a 2:1 pyridine-ethanol solution and 30.0 g (0.43 mole) of hydroxylamine hydrochloride. The mixture was stirred thoroughly and then heated at reflux on a steam bath. A whitish precipitate was observed after one hour of reflux. After two hours of reflux, the reaction was stopped and the solvent removed on a rotary evaporator at a temperature of 60°. To the sludge formed, was added with vigorous stirring 300 ml of a 4:1 water-ethanol solution. The solution cleared and then an off-white precipitate formed. After the precipitate was filtered and washed thoroughly with water, the yield was 32.3 g.

The synthesis from α -pyridil was carried out in the same manner, using 30.0 g (0.14 mole) of the diketone. The yield was 32.7 g.

2) Separation of the Oximes

The large difference in the solubilities of the two isomers in hot ethanol served as a preliminary method of separation. The crude synthesis product was stirred for 10 minutes in 700 ml of boiling ethanol. At the end of this

time, the insoluble material was filtered from the hot solution and recrystallized twice from 800 ml of hot ethanol. There was obtained 4.1 g of white crystals, mp 233 - 234°. Analysis calculated for $C_{12}H_{10}N_4O_2$: C, 59.49%; H, 4.16%; N, 23.13%. Found: C, 59.23%; H, 4.09%; N, 22.85%.

The second isomer was isolated from the filtrate in pure form by two means. In the first method, (a), the filtrate was evaporated to 250 ml by warming under a stream of air, and the resulting precipitate was filtered and redissolved in 200 ml of ethanol by the addition of 1:1 hydrochloric acid until the solution clarified. This solution was added to a hot, ammoniacal solution of nickel (II), cooled to room temperature and the resulting dark red precipitate was filtered and washed thoroughly with a 10% ammonium hydroxide solution. The precipitate was then resuspended in 800 ml of water and 250 g of sodium cyanide was added with stirring. The resulting yellow solution was adjusted to a pH of 8.0 with hydrochloric acid. The white precipitate formed was quickly filtered and washed thoroughly with large amounts of water. It was then dissolved in a minimal amount of hot dimethylsulfoxide. This solution was filtered hot and an equal volume of water was added. The white precipitate that formed was filtered, washed with water and dried. There were obtained 10.2 g

of white crystals, mp 264 - 265°. Analysis calculated for $C_{12}H_{10}N_4O_2$: C, 59.49%; H, 4.16%; N, 23.13%. Found: C, 59.24%; H, 4.32%; N, 23.42%.

In method (b), the filtrate was evaporated to a small volume and the precipitate formed was repeatedly recrystallized from ethanol to a constant melting point. There were obtained 0.6 g of white crystals, mp 264 - 265°.

Separations were carried out on the product of the α -pyridil synthesis in the same manners as above. This resulted in 3.8 g of crystals, mp 233 - 234°, 9.5 g of crystals, mp 264 - 265°, using method (a), and 0.75 g of crystals, mp 264 - 265°, using method (b).

3) Synthesis from 2,2'-Dipyridil- α -monoxime

To a 100-ml round bottom flask, equipped with a reflux condenser, was added 5.0 g (0.021 mole) of 2,2'-dipyridil- α -monoxime, 50 ml of a 2:1 pyridine-ethanol solution and 5.0 g (0.072 mole) of hydroxylamine hydrochloride. The mixture was heated at reflux for two hours on a steam bath, evaporated to 50 ml and 100 ml of water added. There was obtained 4.5 g of white crystals, mp 263 - 264° and 0.4 g of white crystals, mp 193 - 194°.

CHAPTER III

RESULTS AND DISCUSSION

Infrared, nuclear magnetic resonance and ultraviolet spectra were run on the isomers in order to compare them and effect a determination of their individual configurations. Their reactions with nickel (II) were also studied for the same reasons. Table I outlines the results of the IR, NMR and UV spectra obtained for the isomers.

Kleinspehn et al. (13) have shown that the NMR spectra of oximes in dimethylsulfoxide exhibit sharp hydroxyl proton resonance signals whose chemical shifts are essentially concentration independent and thus characteristic of the particular oxime. This phenomenon has also been observed in the NMR spectra of alcohols (14) and phenols (15) in dimethylsulfoxide.

Symmetrical glyoximes can exist in three non-equivalent isomeric configurations. These configurations are known to give different chemical shifts for the hydroxyl protons in their NMR spectra in dimethylsulfoxide (13, 16). The α and β configurations of glyoximes give singlet hydroxyl proton signals with an integration of two protons

TABLE I

SPECTRAL DATA ON THE ISOMERS

OXIME mp	233 - 234 ^o	264 - 265 ^o
Chemical shift of OH protons	Singlet 11.70 ppm	Singlet 11.50 ppm
UV maxima and molar absorbancy index	235 nm 14600	241 nm 8600 276 nm 14500
Characteristic IR bands cm ⁻¹	1485 sh 1290 1158 1099 1010 988 900	1479 1296 sh 1288 sh 1279 1162, 1155 1103, 1098 1004, 997 968 946

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due to their symmetries, while the α isomer gives a doublet hydroxyl proton signal due to the unsymmetrical nature of the configuration (16).

The two isomers of 2,2'-dipyridylglyoxime which were isolated gave only singlets having an integration equal to two protons in their NMR spectra (Table I). This eliminates the possibility of either isomer having the α configuration. It then only remains to determine which isomer is α and which is β .

α -Glyoximes are known to give characteristic reddish-coloured precipitates with nickel (II), while β -glyoximes do not exhibit this chemical characteristic (4, 17). The compound, mp $264 - 265^{\circ}$, gave a red precipitate with nickel (II) while the compound, mp $233 - 234^{\circ}$, gave only a reddish-coloured solution and no precipitate. This fact was used as the basis for one of the methods of isomer purification. 2,2'-Dipyridylketoxime (III), which can be considered to be an analogue to the β form of the glyoxime in its chelating characteristics, gives also a reddish-coloured solution in reaction with nickel (II), but no precipitate (18).

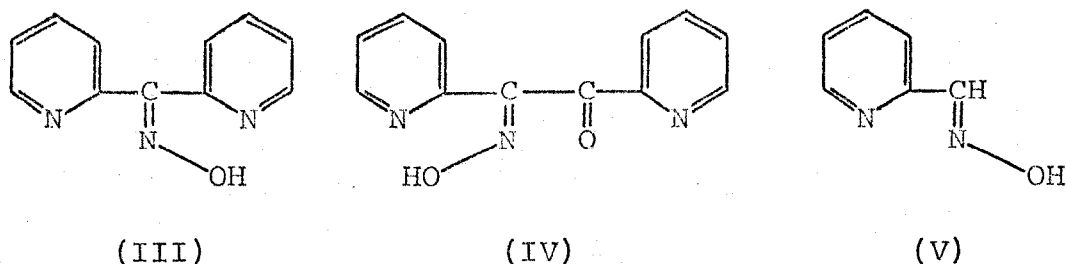
The two isomers can also be compared with each other and other pyridine oximes in the N-O stretching region of the infrared, $900 - 1050 \text{ cm}^{-1}$ (19). Table II lists the absorption bands of a series of pyridyl oximes in this region.

TABLE II

INFRARED COMPARISON DATA

(900 - 1050 cm^{-1})

Compound mp 264 - 265°	Compound mp 233-234°	2,2'-Dipyridyl- α -monoxime	Dipyridyl- ketoxime
1004 cm^{-1}	1010 cm^{-1}	1003 cm^{-1}	1017 cm^{-1}
997	988	993	1001
968		958	969
946		936	950



Three of the four compounds listed have a characteristic set of four bands at approximately the same frequencies in this region. 2,2'-Dipyridylkeoxime (III) and 2,2'-dipyridil- α -monoxime (IV) (20) both have a C=N-OH configuration which places the oxime hydrogen next to the pyridine nitrogen, allowing the possibility of hydrogen bonding. This set of four bands is in contrast to the set of two bands found in this region for the isomer, mp 233 - 234^o. Pyridine-2-aldoxime (V), which has been shown to exist in the syn configuration (21), has also a simple spectra in this region -- one strong band at 980 cm⁻¹ (11).

The reaction of 2,2'-dipyridil- α -monoxime (IV) with hydroxylamine gave as the predominant product, 90% yield, a dioxime, mp 263 - 264^o, plus some unreacted monoxime. Such a reaction should give either the α or γ forms of the glyoxime, but not the β configuration in any major yield.

It is known that less stable isomeric forms of a compound can be, in many cases, converted to the more stable isomer by heating (22). An investigation of molecular models of the α and β isomers of 2,2'-dipyridyl-

glyoxime shows that the α form with its possibility of hydrogen bonding, and thus stable ring formation, should be more thermally stable than the molecularly crowded β form.

Upon heating the lower melting isomer above its melting point, a solid reforms which subsequently melts at a temperature of 263 - 264°.

CHAPTER IV

SUMMARY AND CONCLUSIONS

Two glyoximes have been isolated from the reaction of either α -pyridoin or α -pyridil with hydroxylamine. The melting points, IR, NMR, UV and chemical data show that they are different. On the basis of NMR spectra, the possibility of the γ configuration for either isomer is ruled out.

The glyoxime, mp $264 - 265^{\circ}$, precipitates nickel and has a spectrum in the N-O stretching region of the infrared, which is similar to those of a series of model compounds in which the oxime hydrogen is placed next to the pyridine nitrogen. The isomer, mp $233 - 234^{\circ}$, does not precipitate nickel. Its infrared spectrum in the N-O region differs from the model compounds and is similar to that of syn-pyridine-2-aldoxime.

Reaction of 2,2'-dipyridil- α -monoxime with hydroxylamine yields an oxime, mp $263 - 264^{\circ}$. The isomer, mp $233 - 234^{\circ}$, shows less thermal stability than the isomer, mp $264 - 265^{\circ}$.

From the evidence it is reasonable to conclude that the isomer, mp $264 - 265^{\circ}$, is the α configuration of 2,2'-

dipyridylglyoxime and the isomer, mp $233 - 234^{\circ}$, is the β configuration.

An abstracted portion of the work has been previously published (23).

PART II

ANALYTICAL APPLICATIONS OF

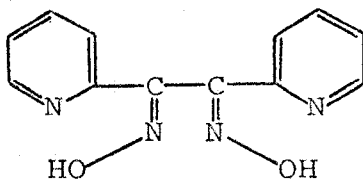
2,2'-DIPYRIDYL- α -GLYOXIME

CHAPTER I

GENERAL INTRODUCTION

α -Glyoximes form stable complexes with a number of the transition metals and so are widely used in the detection and estimation of these metals. Under the conditions used, these reagents are usually highly selective. An example of this high selectivity is the use of the classical chelating agent dimethylglyoxime for the determination of palladium and nickel, determinations in which there are no interferences under the conditions used.

A large number of α -glyoximes have been proposed as analytical reagents. Some of the more widely known examples, besides DMG, are: α -furildioxime, heptoxime, benzildioxime and 4-methylcyclohexane-1,2-dioxime (5). The purpose of the present work was to investigate a new α -glyoxime, 2,2'-dipyridyl- α -glyoxime



with respect to its application to the spectrophotometric determination of trace amounts of metal ions.

The basis of spectrophotometric determination is the absorption of light by a solution. The constituent to be determined is chemically treated in such a manner that it strongly absorbs light (24, 25). If a beam of light is passed through the solution some wavelengths of the light will be absorbed to a greater extent than others and thus, the solution will appear coloured to the eye. The importance of this colouration resides in the fact that the radiation absorbed is characteristic of the compound doing the absorbing. In the ultraviolet and visible regions of the spectrum, this absorption depends, for the most part, upon the number and arrangement of the electrons in the absorbing molecules or ions. The absorption arises from transitions between two different electronic energy levels in the molecule (26). The absorption is differential because of the fact that only discrete amounts of energy can be utilized by the molecule in its electronic transitions, thus the wavelength of absorption is determined by the energy difference involved in the transitions. In inorganic substances, this differential absorption comes about as a result of an unfilled electronic energy level which is covered or protected by a completely filled energy level, which is usually formed by means of coordination with other atoms.

In the practice of spectrophotometry, there are two

laws which are fundamental to quantitative analysis. The first law is the Lambert law which states that when a beam of monochromatic parallel light enters an absorbing medium, the decrease in radiant power (P) with the length of the light path (b) is proportional to the radiant power of the beam. Thus,

$$-\frac{dP}{P} = kdb.$$

On integration, and setting $P = P_0$ when $b = 0$, this yields:

$$\ln \frac{P_0}{P} = kb$$

or

$$P = P_0 e^{-kb}.$$

Beer's law states that the decrease in the radiant power of a beam of parallel monochromatic radiation with the concentration (C) of the absorbing species is proportional to the radiant power of the beam. Thus, similar to Lambert's law.

$$\ln \frac{P_0}{P} = k'C$$

or

$$P = P_0 e^{-k'C}.$$

The two laws may be combined with one constant:

$$P = P_0 e^{-a'bc}.$$

This resolves upon taking logs and changing to the base 10 into:

$$A = \log \frac{P_0}{P} = abc,$$

where A is the absorbance, a is the absorptivity, b is the path length in cm and c is the concentration of absorbing substance in g/l. If c is expressed in moles/l, then the statement of Lambert-Beer law becomes

$$A = \epsilon bc,$$

where ϵ is the molar absorptivity ($l \text{ mole}^{-1} \text{ cm}^{-1}$).

There are several points which should be considered in the investigation of any spectrophotometric procedure in order to optimize it for quantitative analysis. First, the colour-forming reaction should be made as selective as possible by the use of masking and extraction procedures. Secondly, the reagent and the coloured product should be stable for a reasonable length of time. Thirdly, the effects of excess reagent, pH, temperature, formation time and diverse ions should be well known. Next, the system should be highly reproducible and should conform to Beer's law for ease of calibration. Lastly, the molar absorptivity should be reasonably large.

Spectrophotometry affords the chemist a powerful tool in the trace analysis of constituents in a substance. The popularity of spectrophotometric methods arises from five advantages: the apparatus requirements are modest, the

methods are easily used by the average analyst, normally it is rapid, it is highly sensitive and it is as accurate as any other method in its sensitivity range, if not more so (27).

CHAPTER II

SPECTROPHOTOMETRIC DETERMINATION

OF PALLADIUM (II)

A. INTRODUCTION

A large number of reagents and methods have been proposed for the spectrophotometric determination of palladium (II). A number of critical review articles have been written discussing some of these (28, 29, 30). Boltz (31, 32) has recently reviewed a number of new spectrophotometric reagents proposed for the determination of palladium in the period from October 1965 to November 1969. Among these are arsenazo III, or palladiazao (33), isonitrosoacetophenone (34) and dimethylsulfonazo III, which was proposed by Budesinsky and Menclova (35).

α -Glyoximes have long been of interest for the spectrophotometric and gravimetric determination of palladium. This wide interest has arisen from the fact that α -glyoximes are the only reagents for any metals which approach specificity. Dimethylglyoxime is the classical reagent for palladium and has long been used for the gravimetric and the spectrophotometric determination of the metal (36); however, it suffers

from low sensitivity. α -Furildioxime was used by Menis and Rains (37) for palladium. Much emphasis is placed upon the order of reagent addition, solution temperature and the upper limit of the palladium concentration. Also, colour stability is poor. 4-Methyl-1,2-cyclohexanedione-dioxime was used by Banks and Smith for spectrophotometric palladium determination (38). Yet, the method is time consuming being based on prior complex precipitation. α -Benzildioxime has also been used, but this method is handicapped by the fact that readings must be taken in the ultraviolet (280 nm) where there can be a large number of interferences.

In recent years, there has been much interest in pyrildyloximes as reagents for palladium. Sen (39) has proposed phenyl- α -pyridylketoxime as a reagent for palladium; however, the determination must be made in basic media where there is the possibility of precipitation of palladium and consequent low results. Pyridine-2-aldoxime has been suggested, yet a large number of other metal ions interfere (40). Bozic and Holland have proposed 2,2'-dipyridylketoxime as a reagent for both the spectrophotometric (41) and gravimetric (42) determination of palladium (II).

In the present work, 2,2'-dipyridyl- α -glyoxime was

investigated as a reagent for the spectrophotometric determination of microgram amounts of palladium (II).

The reagent reacted with palladium under acidic conditions to form a yellow water-soluble chelate which was easily extracted into chloroform.

The purpose of the present work was to investigate a compound which was both a pyridine oxime and an α -glyoxime, with respect to its use in the spectrophotometric determination of palladium.

B. EXPERIMENTAL

1) Apparatus

Absorbance measurements were made with a Hitachi Perkin-Elmer Model 139 spectrophotometer and a Beckman DB spectrophotometer equipped with a Wavelength Drive Unit and a Sargent Model SRL recorder in 1.00 cm matched silica cells. A Sargent Model LS pH meter equipped with Corning electrodes was used for pH measurements. Class A volumetric glassware was used.

2) Reagents

a) 2,2'-Dipyridylglyoxime Solution

A 1% w/v solution of the glyoxime, mp 259 - 260°, was prepared by adding the glyoxime to 75 ml of 95% ethanol and introducing 1:1 hydrochloric acid dropwise until the solution became clear. This was then diluted to 100 ml with ethanol.

This solution was stable indefinitely in the dark at room temperature and for three weeks in the light. A slight precipitation of reagent can be ignored.

b) Palladium (II) Solution

A stock solution of palladium (II) was prepared by dissolving anhydrous palladium (II) chloride (Fisher Scientific) in concentrated hydrochloric acid, diluting

to 1.0 liter with distilled water and standardizing the solution with 2,2'-dipyridylketoxime (43). Standard solutions were made by appropriate dilutions of the stock solution.

c) Diverse Cation Solutions

These were prepared from reagent grade chloride or nitrate salts. Arsenic, molybdenum, rhenium, tungsten and selenium solutions were prepared from the corresponding oxides.

d) Diverse Anion Solutions

These were prepared from reagent grade sodium or potassium salts.

e) Solvents

A.C.S. grade solvents and distilled water were used in all cases.

3) Recommended General Procedure

An aliquot of sample solution containing 50 to 600 μ g of palladium (II) was placed in a 100-ml beaker. To this were added masking agents, if needed, and 3.0 ml of reagent solution. The pH was adjusted to between 2.8 and 3.3 by the addition of either dilute hydrochloric acid or dilute potassium hydroxide solution. The colour was

allowed to develop for 20 minutes. Then the solution was transferred to a separatory funnel and extracted twice with 10 ml portions of chloroform. The extracts were filtered through a small plug of glass wool in the stem of the separatory funnel, to remove any water, and caught in a 50-ml glass stoppered graduated cylinder. The plug was washed with a few ml of chloroform after each extraction, the washings being added to the extracts. The volume was made up to 50 ml with chloroform and the absorbance was measured at 404 nm against a reagent blank prepared in the same manner. The amount of palladium (II) was calculated from a previously prepared calibration curve.

C. RESULTS

1) Spectral Characteristics

Using the recommended procedure, the chloroform extract of the palladium chelate exhibited an absorbance maximum at 404 nm having a molar absorptivity of $1.01 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$. All analytical measurements were made at this wavelength. The reagent absorbed strongly below 340 nm, but was transparent at 404 nm (Figure I).

2) Effect of pH

The chelate formed in part and was partially extractible over the pH range 0.5 to 14.0. However, complete extraction and formation was found to take place only over the pH range 2.5 to 4.0 (Figure 2). At pH values greater than 4.0, incomplete extraction was observed and at pH values less than 2.5, chelate formation was incomplete.

3) Effect of Solvents

The effect of different solvents for extraction was investigated by using the recommended procedure for development, and extracting into different solvents. Extraction was considered complete if all the palladium was extracted in two extractions. Complete extraction was observed in the cases of both chloroform and dichloromethane. Partial extraction was observed with carbon

FIGURE 1

SPECTRAL CURVE OF THE
PALLADIUM CHELATE EXTRACTED
INTO CHLOROFORM

1. Palladium Chelate
2. Reagent

FIGURE 1

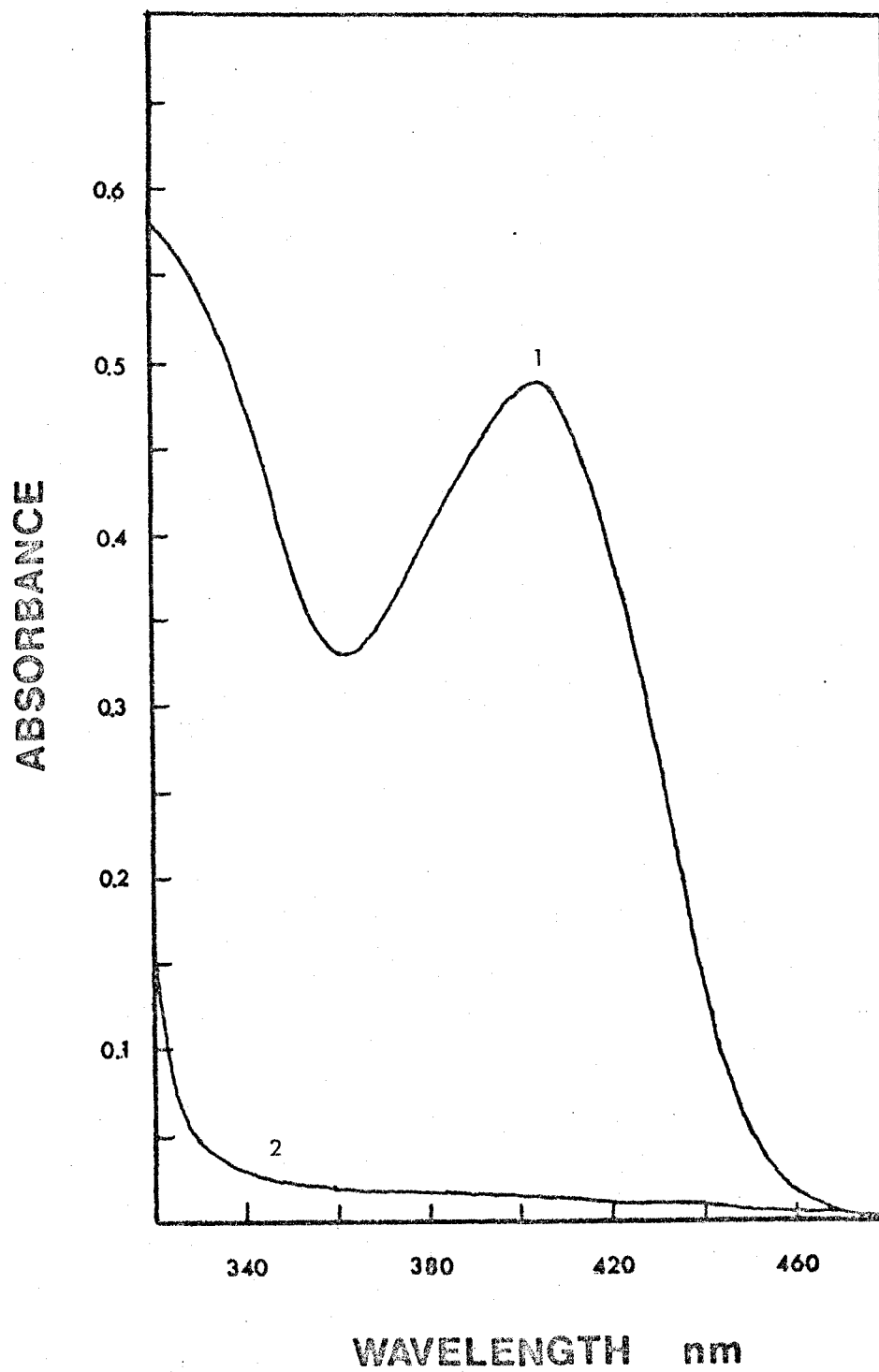
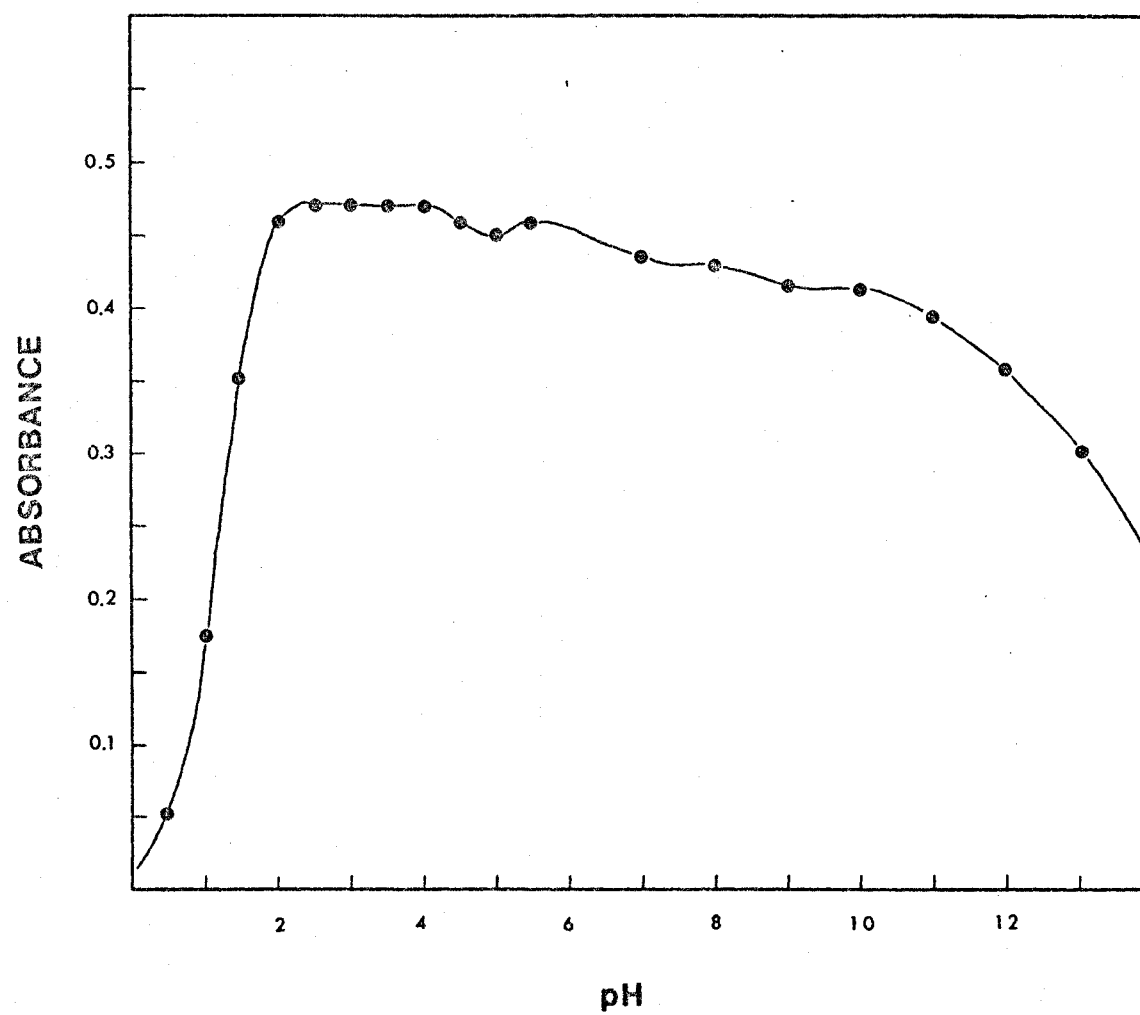


FIGURE 2

EFFECT OF pH ON COMPLEX
FORMATION AND EXTRACTION

FIGURE 2



tetrachloride, benzene and isoamyl alcohol. Large amounts of ethanol, up to 40% by volume, had no effect in either the aqueous phase or the chloroform extract.

4) Effect of Time

The effect of time was studied by extraction after different times under the recommended conditions. The formation of the chelate was found to be complete within 15 minutes (Figure 3). The chloroform extracts were stable for at least 48 hours, if kept in the dark. However, if the extracts are exposed to light for an appreciable length of time, the wavelength of maximum absorbance changes to 398 nm and the absorbance decreases.

5) Effect of Reagent Concentration

It was found that a minimum of 8 moles of reagent for each mole of palladium (II) was needed for complete formation and extraction (Figure 4). Large excesses of reagent did not interfere.

6) Beer's Law Conformity

Conformity to Beer's law was investigated by analyzing aliquots of solution containing differing amounts of palladium (II) using the recommended procedure. A straight line should be obtained over the range in which Beer's law holds. The results of this study were recorded in Table III.

FIGURE 3

EFFECT OF TIME ON THE
FORMATION OF THE PALLADIUM CHELATE

FIGURE 3

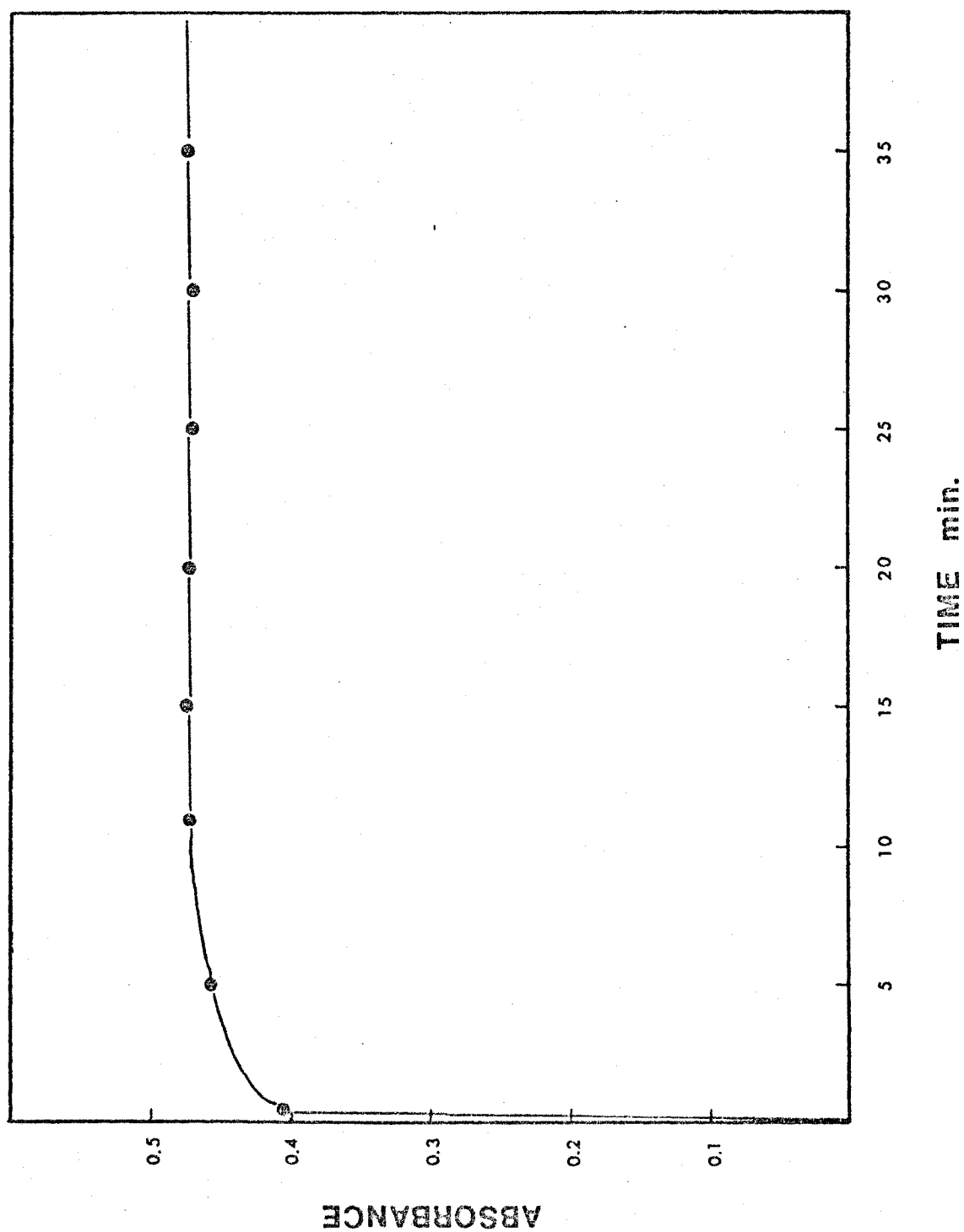


FIGURE 4

EFFECT OF REAGENT CONCENTRATION
ON THE FORMATION AND EXTRACTION
OF THE PALLADIUM CHELATE

FIGURE 4

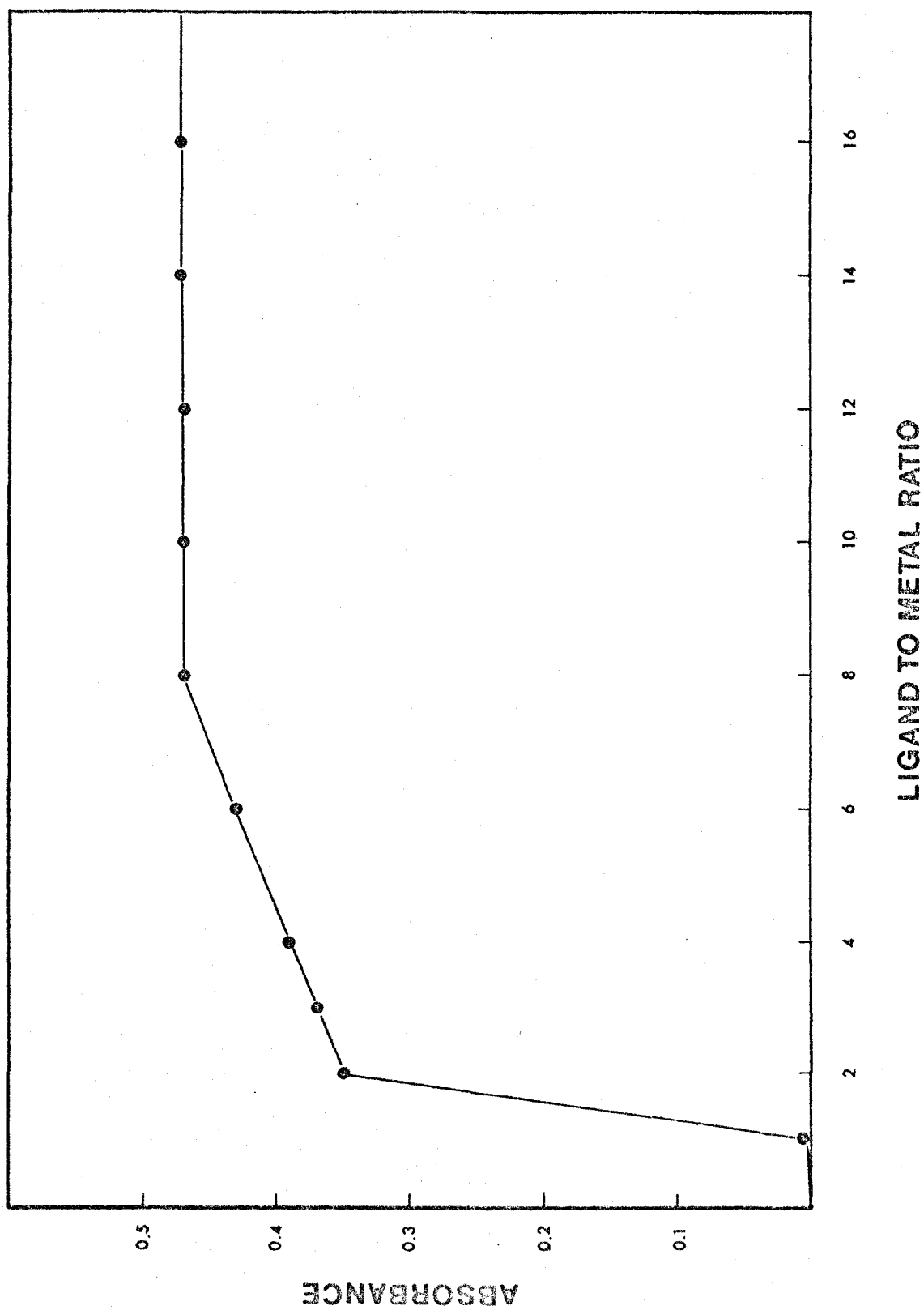


Figure 5 indicates excellent adherence to Beer's law over the concentration range 1 to 13 ppm.

7) Optimum Concentration Range

The optimum concentration range of a spectrophotometric method can be defined by the method proposed by Ringbom (43) and Ayres (44). Percent absorptance ($100 - \%T$) is plotted against the logarithm of concentration. If a sufficient range of concentrations has been covered, an S-shaped curve results. If the system follows Beer's law, the point of inflection occurs at 63% absorptancy. The curve generally has a considerable region which is nearly linear. The extent of this straight portion indicates directly the optimum range of concentration for the particular photometric analysis.

In the present work, the optimum concentration range as evaluated by Ringbom's method was shown to be 2.5 to 8.5 ppm, as illustrated in Figure 6. Table IV presents the data for the plot.

8) Sensitivity

Sandell (45) has defined the sensitivity of a system in terms of the minimum detectable weight of the element. That is, the number of micrograms of element, converted to the coloured product, which in a column of solution having

TABLE III
DATA ON BEER'S LAW
FOR PALLADIUM

Sample	Concentration ppm	Absorbance
1	0.0	0.000
2	1.0	0.094
3	2.0	0.186
4	3.0	0.281
5	4.0	0.375
6	5.0	0.470
7	6.0	0.560
8	7.0	0.653
9	8.0	0.745
10	9.0	0.840
11	10.0	0.932
12	11.0	1.024
13	12.0	1.120
14	13.0	1.212
15	14.0	1.291

FIGURE 5

BEER'S LAW PLOT FOR THE DETERMINATION
OF PALLADIUM WITH 2,2'-DIPYRIDYL- α -GLYOXIME

FIGURE 5

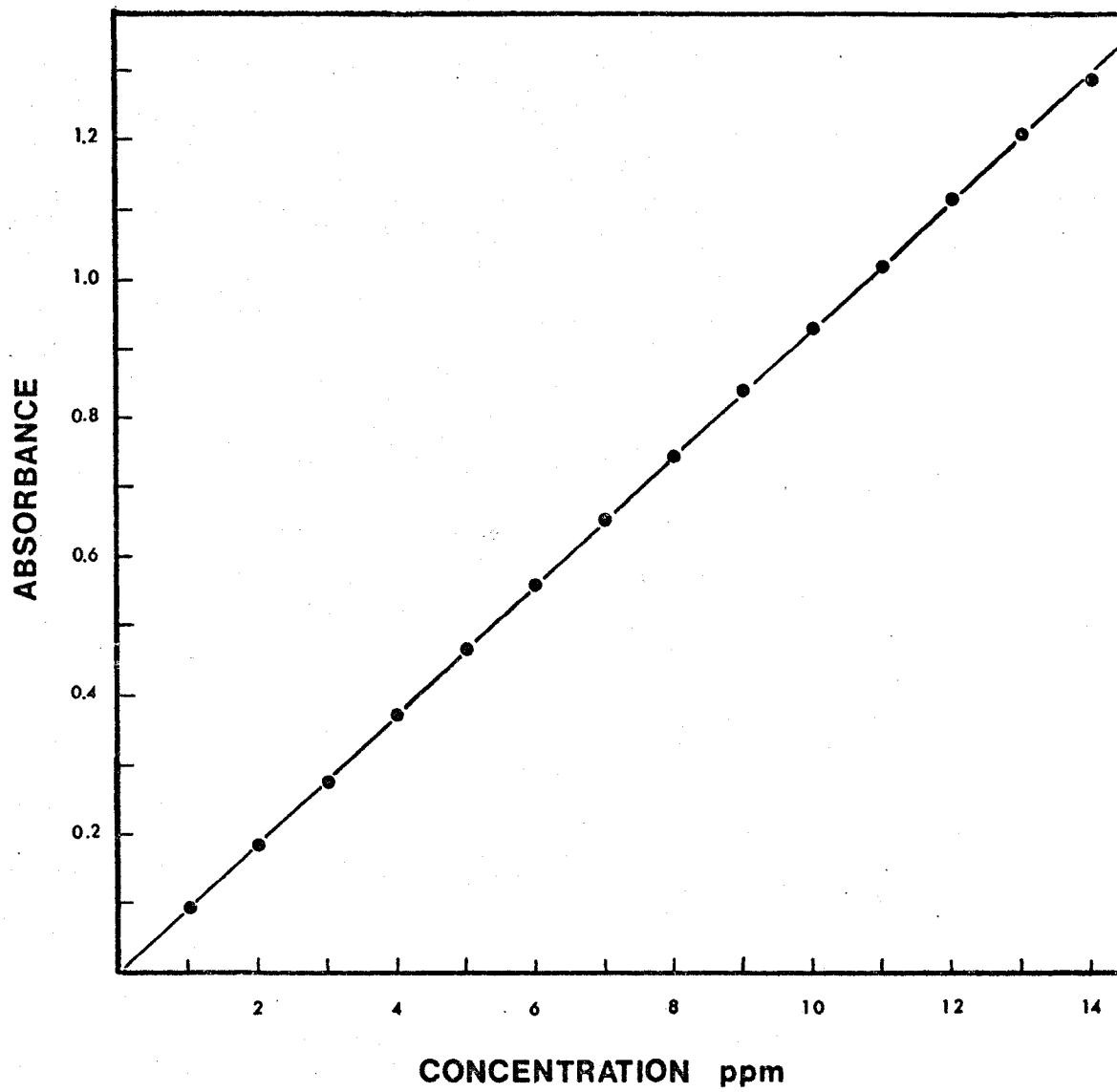


TABLE IV
RINGBOM DATA FOR
PALLADIUM

Absorbance A	Transmittance %T	Absorptancy 100-T	Concentration ppm
0.094	80.6	19.4	1.00
0.186	64.9	35.1	2.00
0.281	52.6	47.4	3.00
0.375	42.2	57.2	4.00
0.470	33.9	66.1	5.00
0.560	27.6	72.4	6.00
0.653	22.2	77.8	7.00
0.745	18.0	82.0	8.00
0.840	14.4	85.6	9.00
0.932	11.7	88.3	10.00
1.024	9.5	90.5	11.00
1.120	7.6	92.4	12.00
1.212	6.1	93.9	13.00
1.291	5.1	94.9	14.00

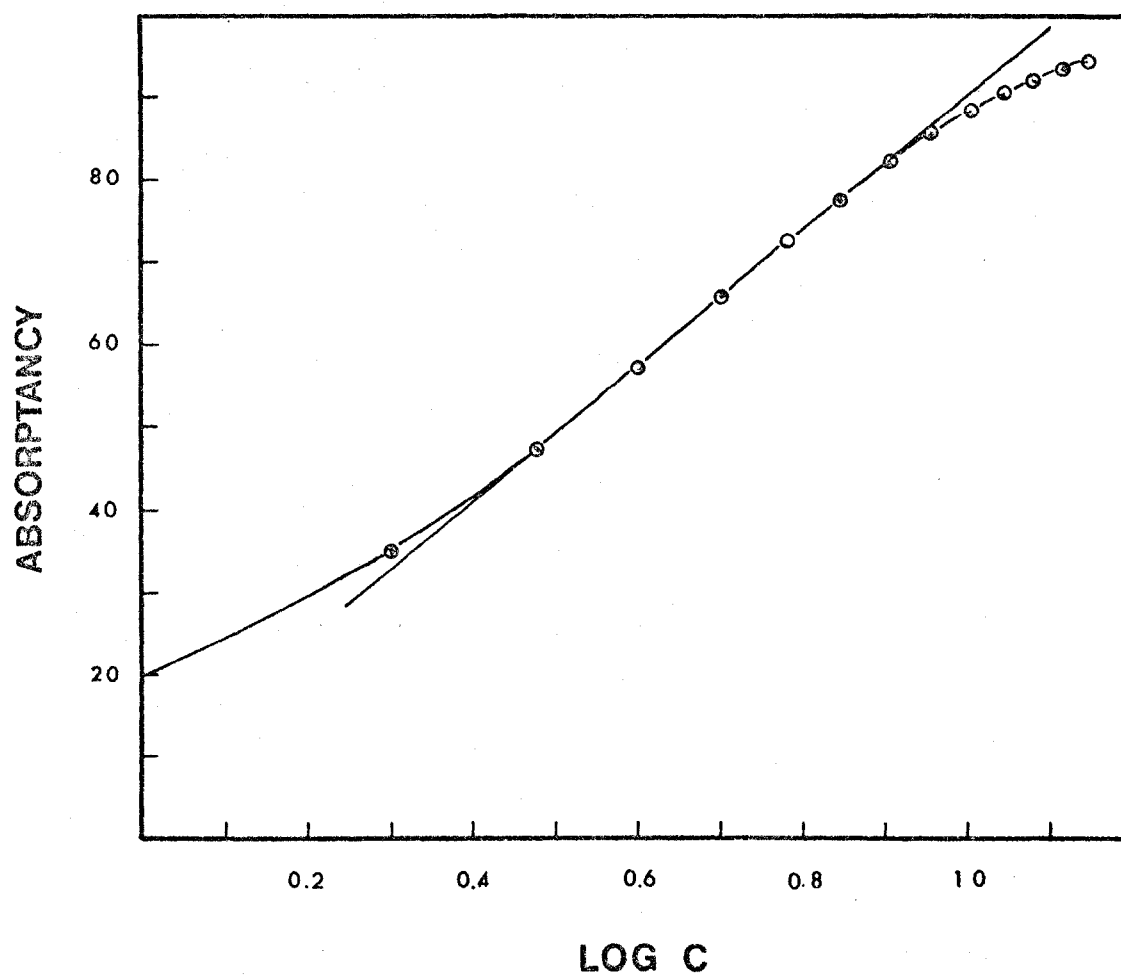
FIGURE 6

RINGBOM PLOT FOR PALLADIUM

DETERMINATION

The optimum concentration range corresponds to the linear portion of the curve.

FIGURE 6



a cross section of 1 cm^2 shows an absorbance of 0.001.

Based on this definition, the sensitivity of the system was found to be $0.011 \mu\text{g cm}^{-2}$.

9) Statistical Study

The precision and accuracy of the system were statistically evaluated by multiple analysis of solutions containing known amounts of palladium (II). Studies were carried out at three different points over the optimum concentration variation. The results of this study were summarized in Table V. The following definitions apply:

Standard Deviation -- the square root of the variance

Variance -- the sum of the squares of the deviations of the results from the mean divided by one less than the total number of results

Relative error -- the mean error of a series of results expressed as a percentage of the two results

Range -- the difference in magnitude between the highest and lowest results in a series

10) Effect of Diverse Ions

The effect of diverse ions was studied by adding 5 mg of a diverse ion to a solution containing 250 μg of palladium (II) and by performing the recommended procedure. An error

TABLE V
STATISTICAL STUDY RESULTS
FOR PALLADIUM*

Experiment	Palladium taken	ppm found	Relative error %	Standard deviation ppm	Range ppm
1	2.00	2.01	0.50	.026	.05
2	5.00	5.00	0.00	.018	.05
3	10.0	10.1	0.60	.075	.09

*Each result is the average of five separate analyses

of 2% in absorbance was considered tolerable. The following ions did not interfere: Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Al^{3+} , As^{3+} , Cd^{2+} , Zn^{2+} , Hg^{2+} , In^{3+} , Ti^+ , Be^{2+} , UO_2^{2+} , Mn^{2+} , Ce^{3+} , EDTA, citrate, F^- , Cl^- , Be^- , ClO_4^- , ClO_3^- , NO_3^- , SO_4^{2-} and PO_4^{3-} . The following did not interfere when masked with 3 ml of 0.1 M EDTA and 5 ml of 10% sodium citrate: Bi^{3+} , Ga^{3+} , V^{5+} , Hf^{4+} , Zr^{4+} , Os^{8+} , Rh^{3+} , Ru^{3+} , Pt^{4+} , Pt^{2+} , Re^{7+} , Sn^{4+} , Se^{4+} , Th^{4+} , Te^{4+} , Ce^{3+} , Pb^{2+} , Cu^{2+} , Cu^+ , Fe^{3+} , Ni^{2+} , Co^{2+} and Ti^{4+} . The system could also tolerate up to 1 mg of Ir^{3+} , Mo^{6+} and Nb^{5+} in the presence of EDTA and citrate. Up to 500 μg of Ag^+ and 250 μg of Au^{3+} could be tolerated. Strong oxidizing agents such as Ce^{4+} , MnO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ interfered and had to be reduced prior to chelation. Sn^{2+} , Fe^{2+} and CN^- all interfered severely and had to be absent.

11) Chelate Composition

Both continuous variations (46) and mole ratio (47) plots indicated that the chelate had a 2:1 ligand to metal ratio under analytical conditions.

12) Reagent Purity

The preceding studies were carried out with a reagent having a melting point of 259 to 260°. Subsequent studies presented in Part I of this dissertation, showed that this

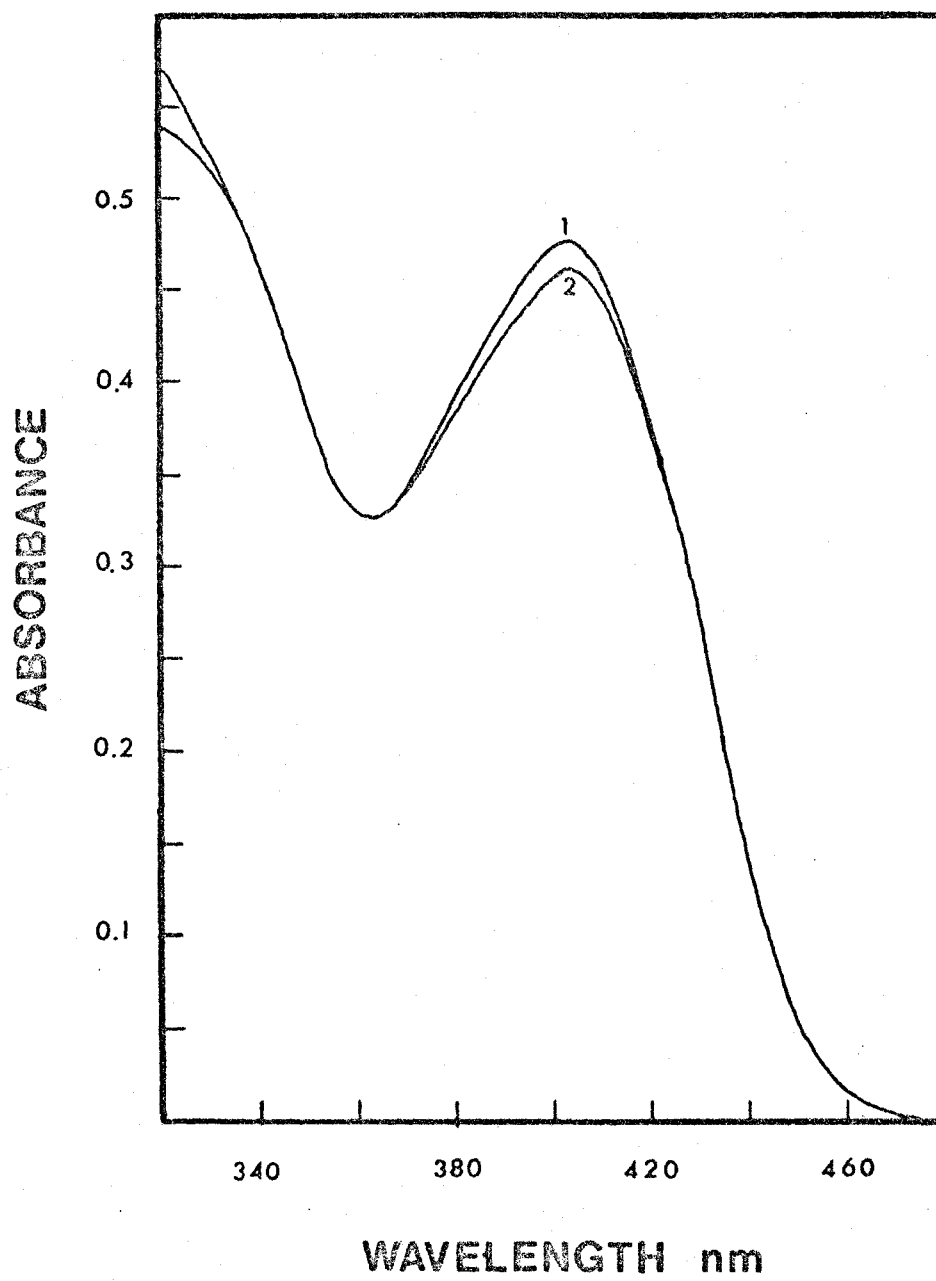
reagent was not pure α -isomer but contained small amounts of β -glyoxime. Thus, a spectral study was initiated to compare the results obtained using a sample of pure α -glyoxime with those using the impure reagent. Figure 7 indicates that there is no observable difference in the spectral characteristics of the palladium chelates of the two compounds.

FIGURE 7

SPECTRAL CURVES OF THE PALLADIUM
CHELATES

1. Pure 2,2'-dipyridyl- α -glyoxime
2. Impure reagent

FIGURE 7



D. DISCUSSION

In the present work, 2,2'-dipyridyl- α -glyoxime has been applied to the spectrophotometric determination of microgram amounts of palladium (II). The platinum group metals do not interfere, milligram quantities of all of them being tolerable in the presence of EDTA and citrate. In all, some 62 diverse ions were tested; of these, only 3 interferences were recorded which required prior separation.

The system is substantially free from critical parameters and Beer's law is obeyed over a wide range of concentration. The method is accurate and reproducible and has good sensitivity.

The ligand to metal ratio in the chelate was found to be 2:1, which is what would be expected for the reaction of an α -glyoxime with palladium (II). Spectral comparison studies indicated that the α -isomer was the active isomer in the reaction.

E. SUMMARY AND CONCLUSIONS

The spectrophotometric determination of palladium (II) with 2,2'-dipyridyl- α -glyoxime involved the extraction into chloroform of between 50 and 600 μ g of palladium as a 2:1 chelate. The extraction was performed on a slightly acid solution after a 20 minute development time. The absorbance of the extract, which was stable for 48 hours in the dark, was measured at 404 nm against a reagent blank. The amount of palladium present was determined from a calibration curve.

A number of parameters were studied in order to assess their effect on the system. These included the effects of pH, solvents, time, reagent concentration, diverse ions and reagent purity, and also Beer's law conformity. Best results were obtained over a pH range of 2.5 to 4.0 after at least a 20 minute development time and a 10 - fold excess of reagent. The number of ions which interfered was very small in the presence of EDTA and citrate, making the method highly selective towards palladium (II).

This procedure compares favourably with existing methods. The small number of interferences and ease of use should make this method applicable to the analysis of complex materials on a routine basis.

An abstracted portion of this work has been previously published (12).

CHAPTER III

SPECTROPHOTOMETRIC DETERMINATION

OF GOLD (III)

A. INTRODUCTION

There are very few spectrophotometric methods for the determination of gold that do not have interferences. The methods which are acceptable for gold normally require some separation from other metals. While there are a number of separation techniques available, one of the best is solvent extraction because it is rapid, simple and gives clean separations.

In 1966, Beamish (48) reviewed the spectrophotometric methods then in use for the determination of gold. With a very few exceptions the methods used involved absorbance measurements on colloidal suspensions or the extracts of these suspensions, or coloured oxidation-reduction products from the reaction of gold with organic materials.

Among the methods mentioned by Beamish were the oxidation of O-tolidine to a coloured product, the formation of a colloid with 5-(p-dimethylaminobenzylidene)-rhodanine, the reduction to colloidal gold by tin (II) chloride, the

extraction of the colloidal rhodamine B complex, the extraction of the colloidal phenyl- α -pyridylketoxime complex and the formation of a dithizonate in organic medium.

Between 1965 and 1969, Boltz (31, 32) has reviewed new methods for the spectrophotometric determination of gold. Among the reagents proposed were: ferroin, pyridine-2-aldoxime, isonicotinic hydrazide and anthranilic acid.

All of the procedures which have been mentioned suffer from two defects. They are all subject to major interferences and great care must be taken in order to ensure reproducible results.

In 1968, rhodamine B was proposed for the fluorometric determination of gold (49). Once again, although the method was highly sensitive, strict control of the parameters had to be observed. Holland and Bozic have proposed 2,2'-dipyridylketoxime as a reagent for the spectrophotometric determination of gold in both aqueous and extraction systems (50). This was the first reagent which formed a water soluble gold complex, solving the problems involved in the measurement of colloidal suspensions.

In the present work, 2,2'-dipyridyl- α -glyoxime has been found to be a selective reagent for the determination of microgram amounts of gold (III) by spectrophotometry.

This reagent reacted with gold (III) over a wide range of pH to form a highly coloured, yellow, water-soluble, stable complex which is extractible into a variety of organic solvents in the presence of excess perchlorate ion.

B. EXPERIMENTAL

1) Apparatus

A Beckman DB spectrophotometer equipped with a Wavelength Drive Unit and a Sargent Model SRL recorder was used for all absorbance measurements, which were made in matched 1.00 cm silica cells. A Sargent Model DR' digital pH meter equipped with a Sargent combination pH electrode was used to obtain pH measurements. Class A volumetric glassware was used.

2) Reagents

a) Standard Gold Solution

A stock solution containing approximately 1 mg/ml of gold (III) was prepared by dissolving $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 3 M hydrochloric acid and diluting to 1.0 liter with distilled water. This solution was standardized by the precipitation of elemental gold with hydroquinone according to the method of Beamish, Russell and Seath (54). The stock solution was further diluted with distilled water to give a standard solution of 30 $\mu\text{g/ml}$. This solution was prepared fresh daily because dilute gold solutions are unstable due to absorption on the walls of glass containers.

b) Reagent Solution

A 1% w/v solution of 2,2'-dipyridyl- α -glyoxime in a 1:1 mixture of ethanol and 0.2 M hydrochloric acid was used. This solution was stable indefinitely.

c) Diverse Cation Solutions

Reagent grade chloride or nitrate salts were used to make solutions containing 5 mg/ml of the diverse ion. Arsenic, molybdenum, tungsten, osmium and selenium solutions were prepared from the corresponding oxides.

d) Diverse Anion Solutions

These were prepared in a concentration of 5 mg/ml from reagent grade sodium or potassium salts.

e) Solvents

A.C.S. reagent grade dichloromethane and methylisobutyl-ketone were used. Fisher certified grade n-amyl alcohol was used. The mixed solvent was a 4:1 v/v solution of dichloromethane and n-amyl alcohol. 95% ethanol and distilled water were used throughout.

3) Recommended Procedure

An aliquot of solution containing between 25 and 275 μ g of gold (III) was placed in a beaker of appropriate size. Three ml of saturated potassium perchlorate solution

and any masking agents needed were added. This was followed by 5.0 ml of reagent solution. The pH was adjusted to between 2.5 and 5.0 by the addition of a few drops of dilute potassium hydroxide or hydrochloric acid solution. The colour was allowed to develop for 10 minutes and the solution was transferred, with washing, to a separatory funnel. The complex was extracted three times with 5 ml portions of the mixed solvent, shaking for one minute for each extraction. The extracts were filtered through a plug of glass wool in the stem of the separatory funnel to remove traces of water. The plug was washed with a small portion of solvent after each extraction. The extracts and washings were added to a 25-ml glass-stoppered graduated cylinder. This was diluted to volume with solvent, and absorbance was measured at 448 nm against a reagent blank prepared in the same manner. The amount of gold present was determined from a previously prepared calibration curve.

C. RESULTS

1) Effect of pH

The effect of pH was studied on both the formation of the complex in aqueous medium and upon the extraction of the complex using the recommended procedure and adjusting pH to different values. The optimum range for formation was 0.5 to 8.0 and the optimum range for extraction was 1.5 to 8.0 (Figure 8).

2) Spectral Characteristics

The aqueous solution of the gold complex exhibited an absorbance maximum at 425 nm, $\epsilon = 1.57 \times 10^4$. Extraction into n-amyl alcohol gave a bathochromic shift to 445 nm, $\epsilon = 1.60 \times 10^4$; into methylisobutylketone gives a shift to 448 nm, $\epsilon = 1.07 \times 10^4$; and into the mixed solvent gives a shift to 448 nm, $\epsilon = 1.80 \times 10^4$. At the wavelengths, there was very little absorbance due to the reagent. The spectra of the aqueous and mixed solvent systems are presented in Figure 9.

3) Effect of Solvents

Using the recommended procedure, the complex was completely extracted (3 extractions) into isobutanol, amyl alcohols, methylisobutylketone, and the mixed solvent. It was partially extracted into chloroform

FIGURE 8

EFFECT OF pH ON COMPLEX

FORMATION AND EXTRACTION FOR GOLD

1. Extraction
2. Complex formation

FIGURE 8

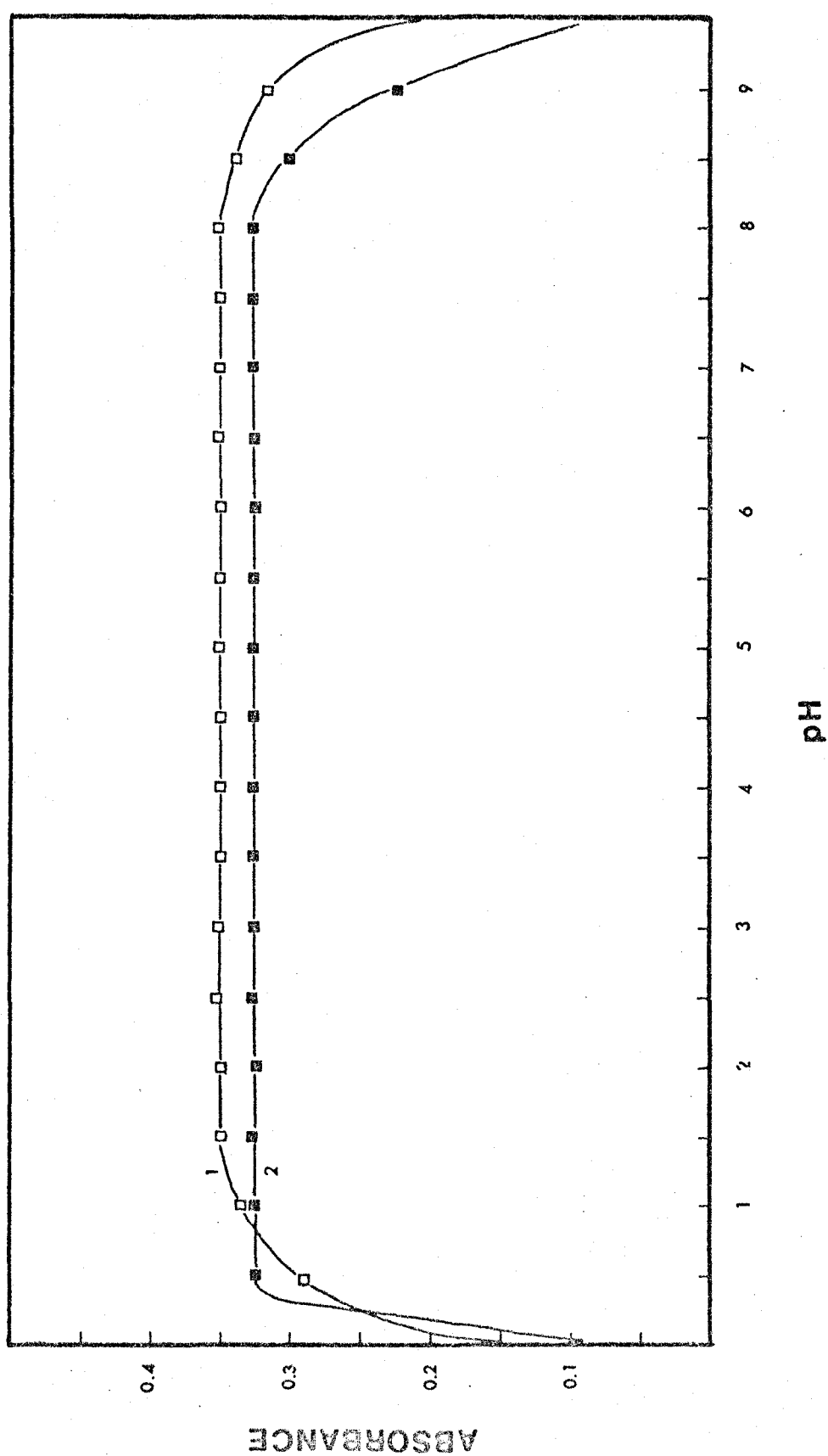


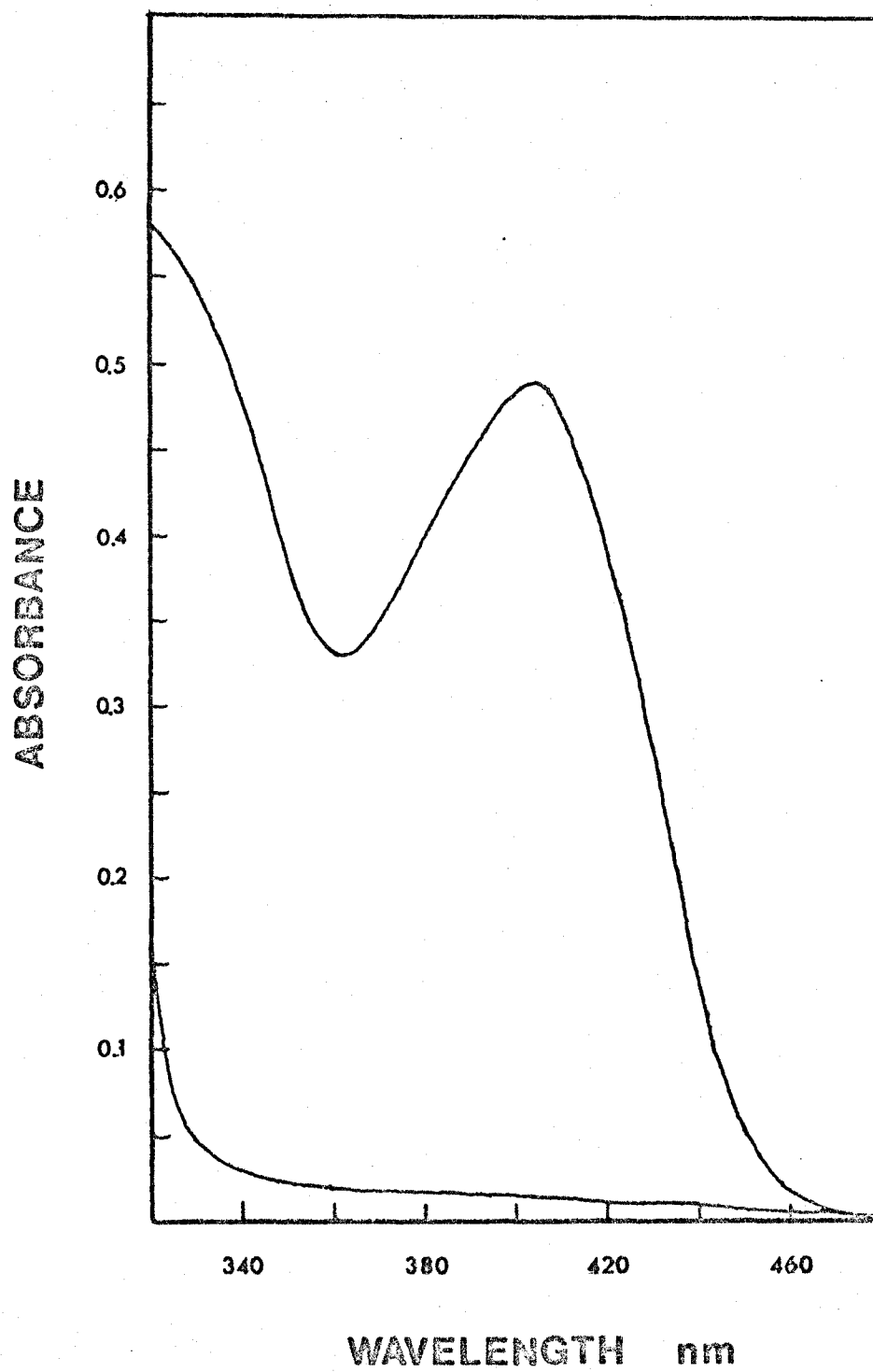
FIGURE 9

SPECTRAL CURVES OF THE

GOLD (III) COMPLEX

1. Reagent
2. Aqueous development
3. Mixed solvent extract

FIGURE 9



and dichloromethane.

4) Effect of Ion-Pair Formation

Using the recommended procedure, the complex was totally extracted in the presence of excess perchlorate, chlorate or nitrate ions and partially extracted in the presence of excess phosphate, sulfate, chloride or acetate ions. When there were no added anions, there was only slight extraction.

5) Effect of Reagent Concentration

A 40:1 molar excess of reagent was required under analytical conditions for satisfactory results. Large excesses of reagent do not interfere.

6) Effect of Time

Complex formation was complete in 40 minutes at a pH of 0.5, in 20 minutes at a pH of 1.0 and in 5 minutes at a pH of 2.0 and above. The extracts were stable for at least 24 hours in the light.

7) Effect of Heating

There was no effect to the system upon heating to 80° after reagent addition.

8) Beer's Law Conformity

Aliquots of solution containing differing amounts of

gold (III) were analyzed using the recommended procedure. Figure 10 and Table VI show excellent adherence to Beer's law from 1.0 to 11.5 ppm.

9) Optimum Range

The optimum concentration range was evaluated to be 2.8 to 8.0 ppm by the Ringbom's method (Figure 11). Table VII shows the data used.

10) Sensitivity

The sensitivity of the extraction system was $0.012 \mu\text{g cm}^{-2}$ as defined by Sandell.

11) Effect of Diverse Ions

The effect of diverse ions was studied by adding 5 mg of a diverse ion to a solution containing $150 \mu\text{g}$ of gold (III) and following the recommended procedure. A variation of 2% in absorbance was considered tolerable. There was no interference from the following ions: Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^+ , Se^{4+} , Cr^{3+} , Mn^{2+} , Hf^{4+} , Zr^{4+} , La^{3+} , Pb^{2+} , UO_2^{2+} , Th^{4+} , Cd^{2+} , Os^{8+} , Pt^{4+} , F^- , Cl^- , Br^- , CrO_4^{2-} , OAc^- , PO_4^{3-} , SO_4^{2-} , ClO_4^- , ClO_3^- , NO_3^- , NO_2^- , and $\text{C}_2\text{O}_4^{2-}$. Citrate and tartrate did not interfere in amounts up to 1 g. Up to 400 mg of EDTA did not interfere if added 10 minutes after the reagent. Up to 3 mg of Re^{7+} as ReO_4^- could be tolerated. Up to 2 mg

TABLE VI
DATA ON BEER'S LAW FOR
GOLD (III)

Sample	Concentration ppm	Absorbance
1	0.00	0.000
2	0.80	0.064
3	1.60	0.133
4	2.40	0.200
5	3.20	0.270
6	4.00	0.342
7	4.80	0.409
8	5.60	0.478
9	6.40	0.548
10	7.20	0.618
11	8.00	0.692
12	8.80	0.761
13	9.60	0.832
14	10.40	0.900
15	11.20	0.972
16	12.00	1.036

FIGURE 10

BEER'S LAW PLOT FOR THE DETERMINATION
OF GOLD (III)

FIGURE 10

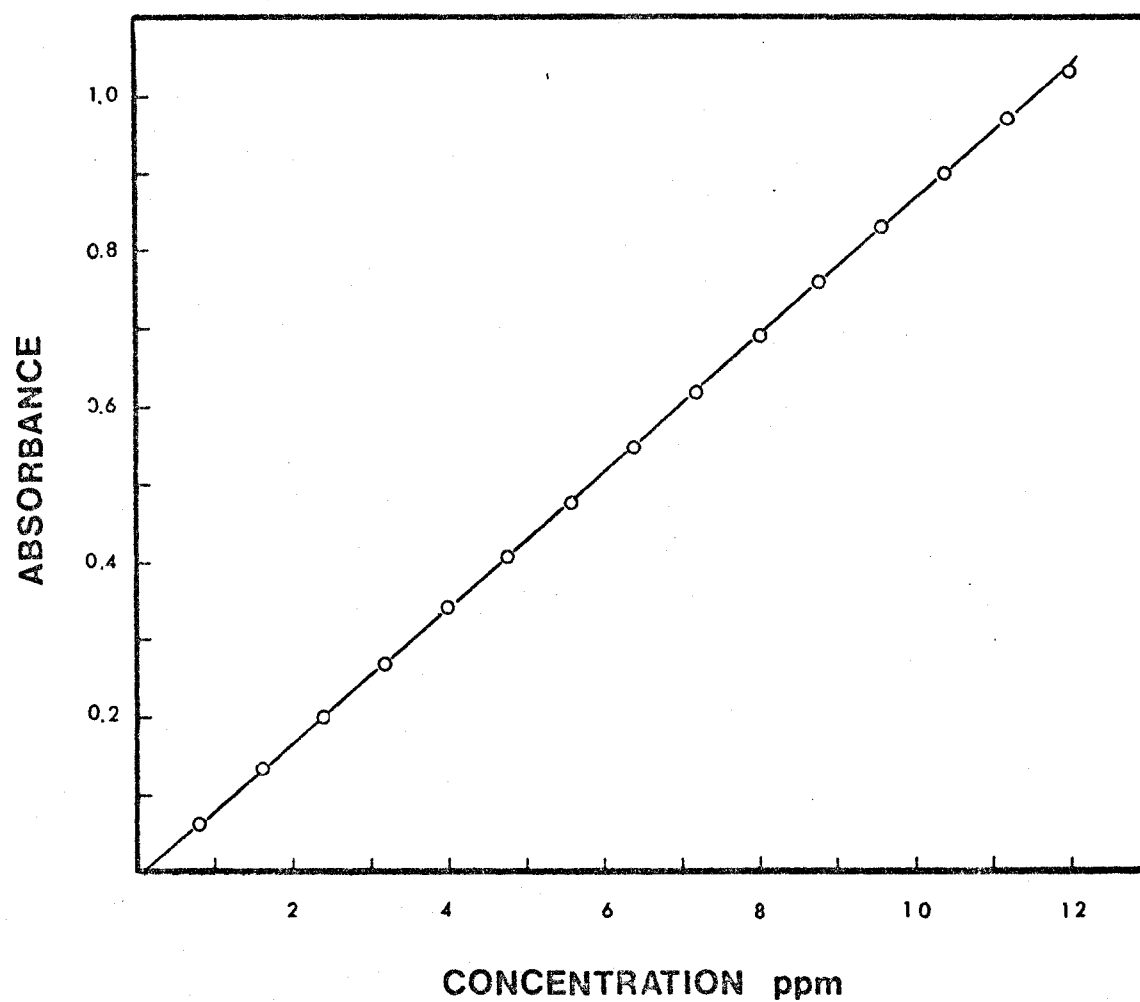


TABLE VII
RINGBOM DATA FOR
GOLD (III)

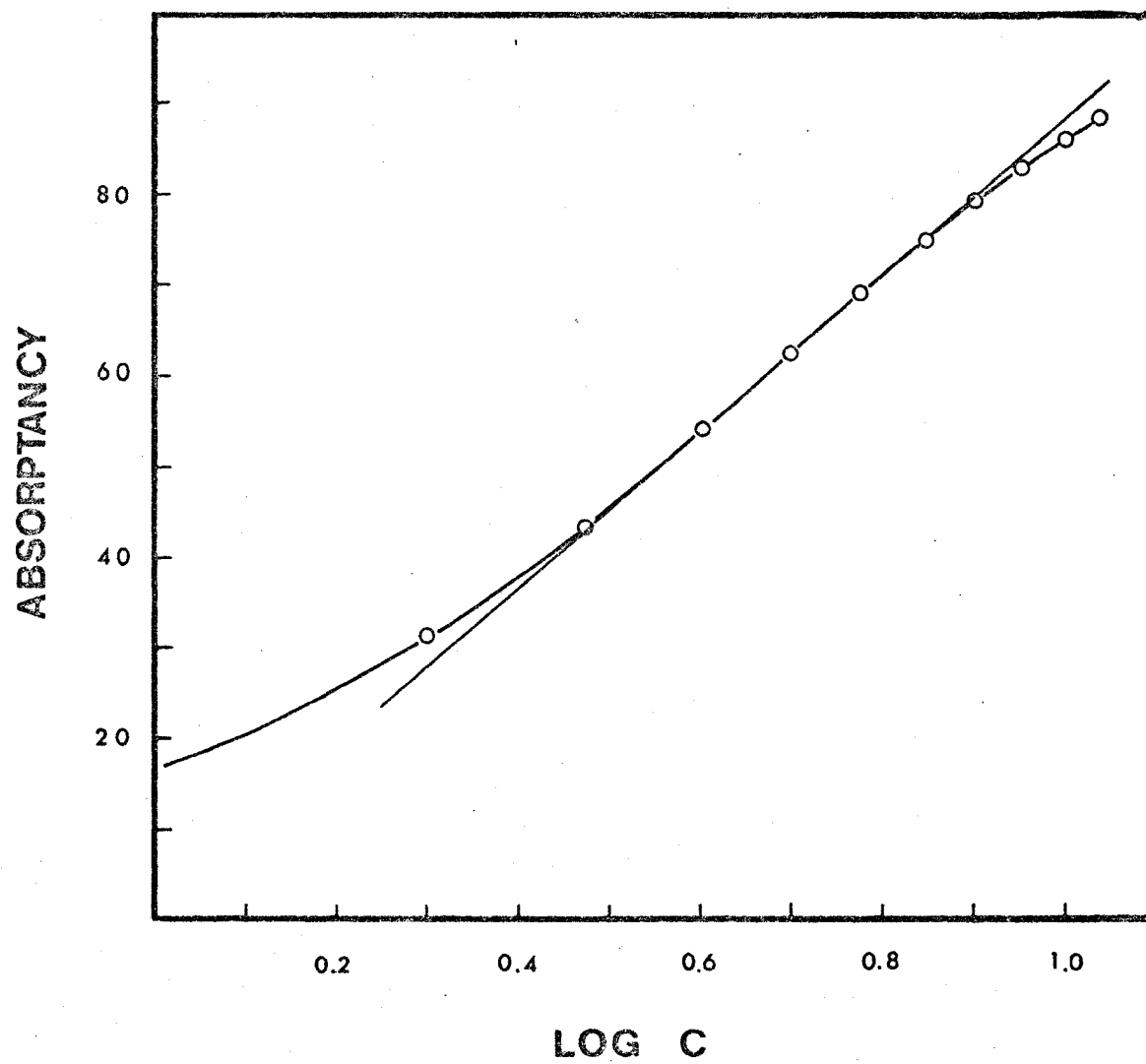
Absorbance A	Transmittance %T	Absorptancy 100-T	Concentration ppm
0.078	83.6	16.4	1.00
0.164	68.4	31.6	2.00
0.251	56.1	43.9	3.00
0.340	45.7	54.3	4.00
0.426	37.5	62.5	5.00
0.513	30.6	69.4	6.00
0.601	25.1	74.9	7.00
0.689	20.4	79.6	8.00
0.778	16.7	83.3	9.00
0.864	13.7	86.3	10.00
0.953	11.1	88.9	11.00

FIGURE 11

RINGBOM PLOT FOR GOLD (III)

DETERMINATION

FIGURE 11



of Ag^+ and As^{5+} did not interfere. The following ions could be masked by the addition of 200 mg of tartrate: Nb^{5+} , Mo^{6+} , Sn^{4+} , W^{6+} , Hg^{2+} , Bi^{3+} , Ir^{3+} , Zn^{2+} , Ce^{3+} , and Te^{4+} . Up to 4 mg of Sb^{5+} could be masked with 200 mg of tartrate. The following ions could be masked by 40 mg of F^- : Fe^{3+} (5 mg), Ti^{4+} (2 mg) and V^{5+} (2 mg) as VO_3^- . Up to 2 mg of Cu^{2+} could be masked by the addition of 100 mg of EDTA after complex formation was complete. Up to 1 mg of Ni^{2+} could be masked in the same manner. The following ions interfere and must be separated beforehand: Sn^{2+} , Pd^{2+} , Co^{2+} , Rh^{3+} , Ru^{3+} , I^- , CN^- and SCN^- .

12) Statistical Study

The precision and accuracy of the system was studied at three ranges of gold concentration by analyzing solutions containing known amounts of gold (III). This method should assess not only any overall system defects but also any defects resulting from concentration effects. The statistical parameters were defined in the palladium study. The results of this study are summarized in Table VIII.

TABLE VIII

STATISTICAL STUDY RESULTS

FOR GOLD (III)*

Experiment	Gold taken	ppm found	Relative error %	Standard deviation ppm	Range ppm
1	2.42	2.43	+0.61	0.018	0.07
2	4.03	4.03	-0.36	0.017	0.06
3	8.05	8.00	-0.75	0.091	0.15

*Each result is the average of 10 separate analyses

D. DISCUSSION

In the present work a procedure for the spectrophotometric determination of gold (III) based upon the extraction of a highly coloured yellow complex has been developed. The water soluble complex formed could be extracted into a number of oxygen containing solvents as an ion association complex with a number of anions. The method was relatively free from interferences.

There were no critical parameters to contend with in the system. This is in contrast to the strict control of experimental conditions which is generally needed in other systems for the spectrophotometric determination of gold.

Complex formation rather than reagent oxidation is supported by four facts. The method worked well in the presence of oxidizing agents which should lead to high results if oxidation were the mode of colour development. The normal methods of determining the ligand to metal ratio could not be applied due to the formation of a series of different coloured products at low reagent concentrations. The coloured product would only extract as an ion-pair in the presence of high concentrations of anions. The presence of other complexing agents for gold gave low results.

E. SUMMARY AND CONCLUSIONS

The spectrophotometric determination of gold described in this dissertation involved the extraction of the complex formed between gold (III) and 2,2'-dipyridyl- α -glyoxime from a solution having a pH between 2.5 and 5.0 as an ion association complex into a mixed solvent consisting of one part n-amyl alcohol and four parts dichloromethane after a 10 minute development time. The absorbance of the extract was measured at 448 nm against a reagent blank.

A number of parameters were investigated. The maximum colour intensity developed between a pH of 0.5 and 8.0. After development, the best extraction was obtained over a pH range of 1.5 to 8.0. A large reagent excess was used; however, excess reagent did not interfere. Colour development was complete in 5 minutes at pH values greater than 2.0 and the colour was stable for at least 24 hours after extraction. The method obeyed Beer's law over a large concentration range. The system proved to be both precise and accurate.

An extensive foreign ion study, some 65 ions, turned up only 8 ions which interfered at the milligram level. This study indicated that the system is possible for use in the rapid analysis of complex gold bearing materials.

An abstracted portion of this work has been accepted

for publication (51).

CHAPTER IV

SPECTROPHOTOMETRIC DETERMINATION

OF IRON

A. INTRODUCTION

Because of its abundance, wide distribution in nature and extensive use in manufactured products, sensitive and precise methods for the trace determination of iron in the presence of large amounts of other constituents are of great interest to the analyst. There are a large number of spectrophotometric reagents for the determination of iron which have been proposed (31, 32, 52, 53, 54). These reagents range in sensitivity and selectivity from the highly sensitive ($\epsilon = 1.47 \times 10^5$) method involving chrome azural and cetyltrimethylammonium chloride as the colour former, to the classical reagent KSCN.

In solution, iron has two principal oxidation states, +2, ferrous and +3, ferric. As Sandell (55) reports, there is no lack of reagents for the spectrophotometric determination of iron, but few are well suited for trace amounts. Some reagents react with ferric iron and others with ferrous. Generally, reagents that react with iron (II)

are preferable to those that react with iron (III) because of the large number of anions which interfere in the determination of ferric iron by the formation of stable ferric complexes.

Although a number of compounds react with iron (II), the formation of stable ferrous complexes is limited, in practice, to ligands which bond through nitrogen atoms (56). The "chelate effect" has a further effect of enhancing stability (57, 58). A number of reagents have been proposed which have both these properties. Among these are 1,10-phenanthroline (59), 2,2'-bipyridine (60), phenyl-2-pyridylketoxime (61), 2,4,6-bipyridyl-s-triazine (62), dimethylglyoxime (63) and 2,2'-dipyridylketoxime (64). All of these compounds contain the atomic grouping $-N=C-C=N-$ which permits the formation of 5-membered chelate rings bonding through the nitrogen atoms.

In the present work, 2,2'-dipyridyl- α -glyoxime, which has the same atomic grouping in the oxime groups, has been applied to the spectrophotometric determination of iron in the ferrous state, based on the formation of a highly coloured, red complex in an alkaline citrate medium. One of the objects of this investigation was to develop a simple rapid procedure for the determination of iron in the presence of large amounts of copper and nickel. A

number of parameters have been investigated in order to determine the optimum analytical conditions.

B. EXPERIMENTAL

1) Apparatus

All spectrophotometric readings were obtained with a Beckman DB spectrophotometer equipped with a Wavelength Drive Unit and a Sargent Model SRL recorder in matched 1.0 cm silica cells. All pH measurements were obtained with a Sargent Model DR pH meter equipped with a Sargent combination pH electrode. Class A volumetric glassware was used.

2) Reagents

a) Standard Iron Solution

A stock iron solution was made from high purity iron wire, 99.95%, obtained from J.T. Baker Chemical Co. The wire was cleaned in hydrochloric acid to get rid of any oxides, washed thoroughly first with distilled water and then with acetone and dried. This was dissolved in dilute hydrochloric acid and diluted to 1.0 liter to give a solution containing 1 mg/ml. This was further diluted with distilled water to give a standard solution containing 30 μ g/ml of iron as the chloride.

b) Reagent Solution

A 1% w/v solution of 2,2'-dipyridyl- α -glyoxime in a 1:1 mixture of ethanol and 0.25 M hydrochloric acid was used

as the reagent. This solution was stable indefinitely.

c) Buffer Solution

The buffer solution was prepared by dissolving 6.8 g of A.C.S. reagent grade ammonium chloride in 60 ml of concentrated ammonium hydroxide (A.C.S. reagent grade) and diluting to 100 ml. This gave a buffer having a pH of 10.5.

d) Diverse Ion Solutions

Cation solutions were prepared from reagent grade chloride or nitrate salts except in the cases of molybdenum, osmium, selenium, tungsten and arsenic which were prepared from the corresponding oxides. Anion solutions were prepared from reagent grade sodium or potassium salts. Masking agents and hydroxylamine hydrochloride solutions were prepared from reagent grade materials.

3) Recommended Procedure

An aliquot of solution containing between 15 and 300 μ g of iron was placed in a beaker of appropriate size. To this were added 2 ml of a 10% hydroxylamine hydrochloride solution, 4 ml of a 250 mg/ml citrate solution and 5 ml of reagent solution. To this was added 15 ml of the buffer. The solution was heated at a boil for 5 minutes, cooled to room temperature in an ice bath, transferred to a 50-ml

glass-stoppered graduated cylinder with washing and diluted to volume. Absorbance was measured at 534 nm against a reagent blank prepared in the same manner. The amount of iron present was calculated from a previously prepared calibration curve.

C. RESULTS

1) Spectral Data

Under the conditions of analysis, the complex had a maximum absorbance at 534 nm with a molar absorptivity of $1.33 \times 10^4 \text{ l mole}^{-1} \text{ cm}^{-1}$ as shown in Figure 12. The reagent itself absorbed strongly below 380 nm, but had little absorbance at the analytical wavelength.

2) Effect of pH

The effect of pH on the system was studied by adjusting the pH with dilute hydrochloric acid or potassium hydroxide solution, waiting 2.5 hours and reading the absorbance of the solution. The optimum pH for formation was between 9.5 and 11.5 as seen in Figure 13. Below a pH of 9.5, there was precipitate formation with consequent low absorbance; above a pH of 11.5, complex formation was incomplete.

3) Effects of Time and Heating

The effects of heating and time were studied by adjusting the pH of the system to between 10.0 and 11.0 with dilute hydrochloric acid or potassium hydroxide and allowing it to stand at room temperature or heating at a boil for a specified period of time. At room temperature, complex formation was complete in 18 minutes. It was found, also, that heating to a boil effected

FIGURE 12

SPECTRAL CURVE OF THE

IRON (II) COMPLEX

1. Iron (II) complex
2. Reagent

FIGURE 12

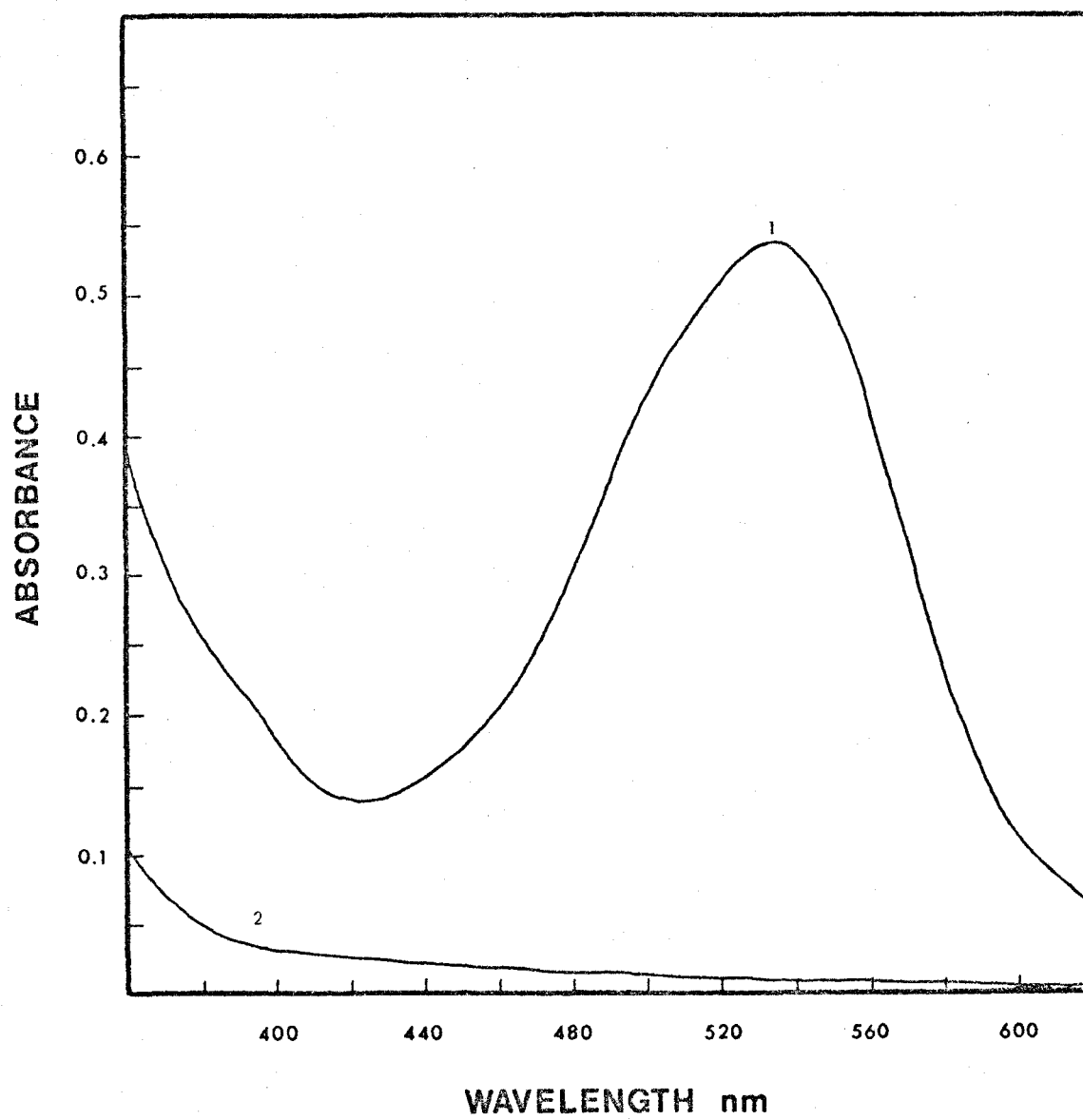
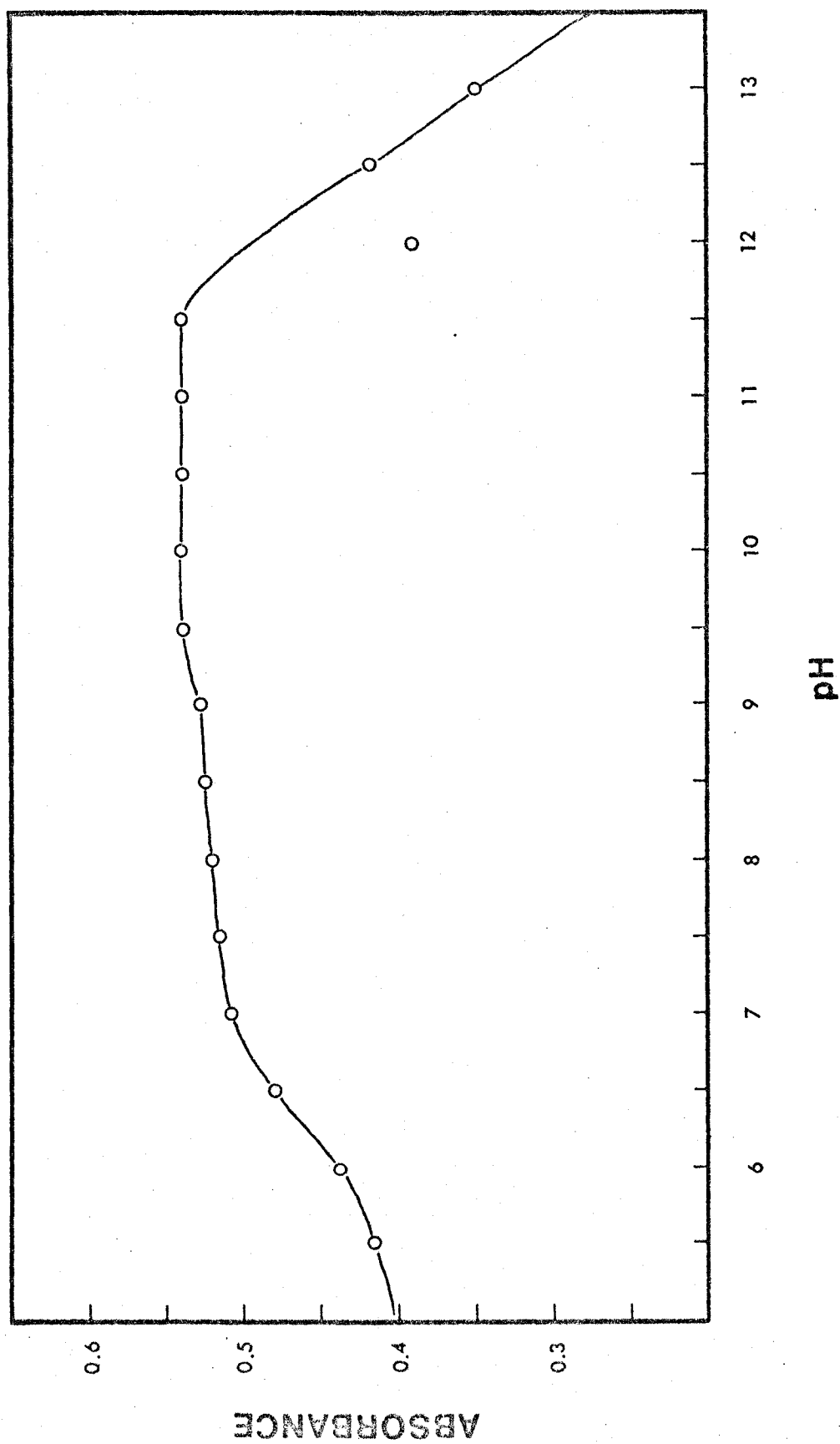


FIGURE 13

EFFECT OF pH ON COMPLEX
FORMATION

FIGURE 13



complete complex formation. The results of this study are presented in Table IX. The complex, once formed, was stable for at least 24 hours in the light.

4) Effect of Buffer

The effect of the buffer was studied by adding the buffer to the system after the other reagents and taking readings after the appropriate manipulations. In the presence of the buffer there was a bathochromic shift in the observed maximum to 560 nm and a lowering of the molar absorptivity. This effect disappeared upon heating the solution at a boil for a period of 5 minutes or more, as indicated in Figure 14.

5) Effect of Reagent Concentration

The effect of reagent concentration was studied by carrying out the recommended procedure at differing molar excesses of reagent. It was found that a 60:1 molar ratio of reagent to iron was required for reproducible results under analytical conditions.

6) Effect of Hydroxylamine Hydrochloride

In order to ascertain whether or not the hydroxylamine hydrochloride added had any function in the system other than to reduce the iron (III) to iron (II), the spectrum of the complex formed between the reagent and ferrous

FIGURE 14

SPECTRAL CURVES OF THE IRON (II)

COMPLEX IN THE PRESENCE OF

BUFFER

1. After heating
2. Before heating

FIGURE 14

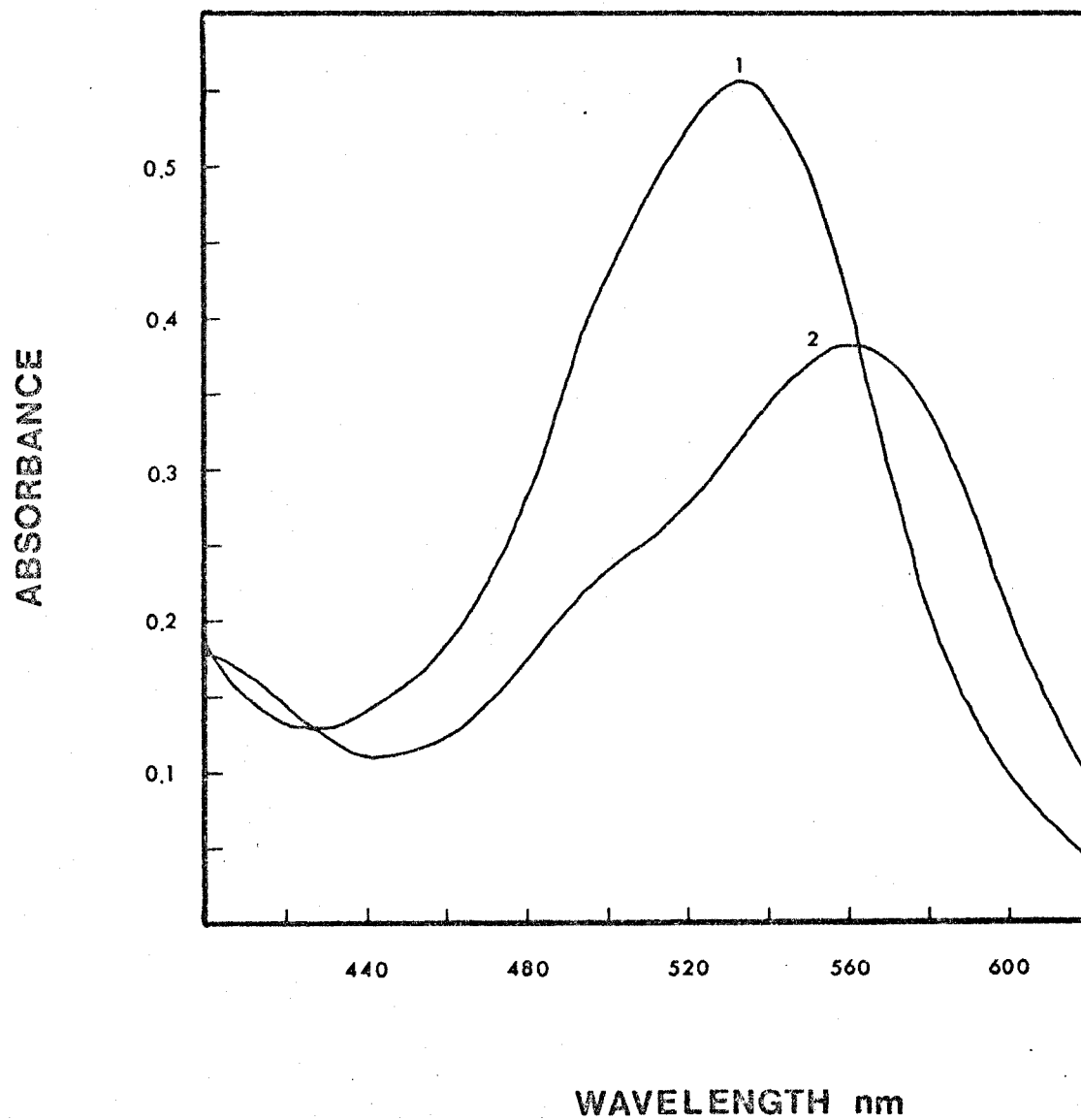


TABLE IX

EFFECT OF TEMPERATURE AND TIME ON THE DEVELOPMENT
OF THE IRON COMPLEX (2.43 ppm iron)

Sample	Conditions	Absorbance
1	No heating; read immediately	0.263
2	No heating; read after 5 minutes	0.460
3	No heating; read after 10 minutes	0.524
4	No heating; read after 15 minutes	0.552
5	No heating; read after 20 minutes	0.565
6	Heat to boil; read immediately	0.559
7	Heat to boil; maintain for 5 minutes	0.565
8	Heat to boil; maintain for 10 minutes	0.565
9	Heat to boil; maintain for 15 minutes	0.567
10	Heat to boil; maintain for 20 minutes	0.565

ammonium sulfate under the conditions of analysis was compared with that obtained in the presence of hydroxylamine hydrochloride. There is no difference between the two systems as shown by the spectra presented in Figure 15.

7) Beer's Law Adherence

The adherence of the system to Beer's law was studied by carrying out the recommended procedure upon aliquots of solution containing differing amounts of iron. As shown by Figure 16 and Table X, Beer's law is obeyed over an exceptionally large concentration range, 0.3 to 6.0 ppm.

8) Optimum Concentration Range

The optimum range of concentration for analysis was evaluated by Ringbom's method. The straight line portion of the curve presented in Figure 17 indicates this range to be from 0.8 to 3.6 ppm. Table XI presents the data from the plot.

9) Sensitivity

The sensitivity of the system as evaluated by Sandell's method was $0.004 \mu\text{g cm}^{-2}$.

10) Statistical Study

The precision and accuracy of the system were studied by performing a statistical analysis on the results

FIGURE 15

SPECTRAL CURVES OF THE IRON (II)
COMPLEX SHOWING THE EFFECT OF
HYDROXYLAMINE HYDROCHLORIDE

1. Hydroxylamine hydrochloride added.
2. Ferrous ammonium sulfate.

FIGURE 15

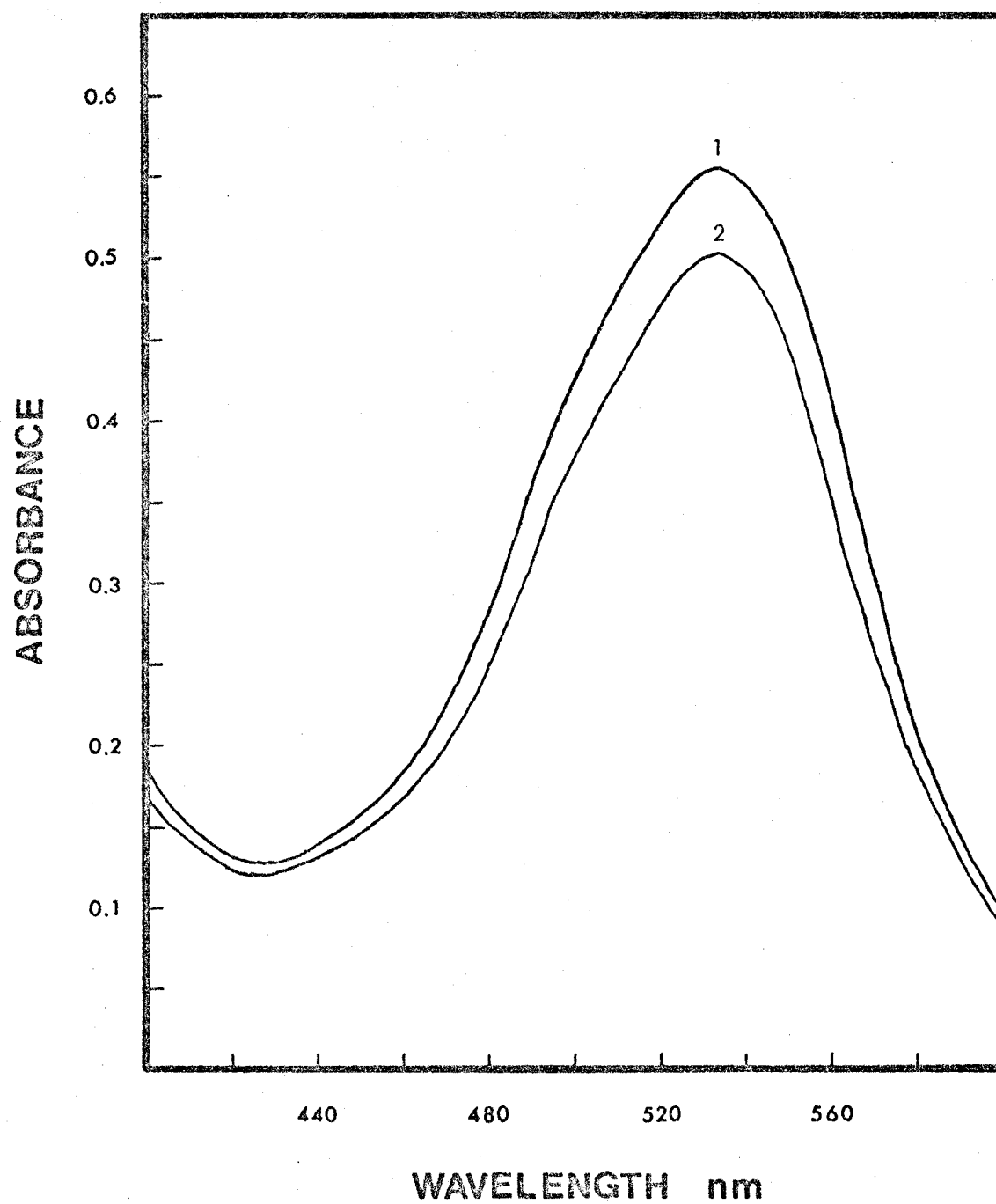


TABLE X
DATA ON BEER'S LAW
FOR IRON (II)

Sample	Concentration ppm	Absorbance
1	0.00	0.000
2	0.30	0.069
3	0.60	0.140
4	1.20	0.281
5	1.80	0.421
6	2.40	0.560
7	3.00	0.700
8	3.60	0.842
9	4.20	0.975
10	4.80	1.114
11	5.40	1.260
12	6.00	1.398

FIGURE 16

BEER'S LAW PLOT FOR THE
DETERMINATION OF IRON (II)

FIGURE 16

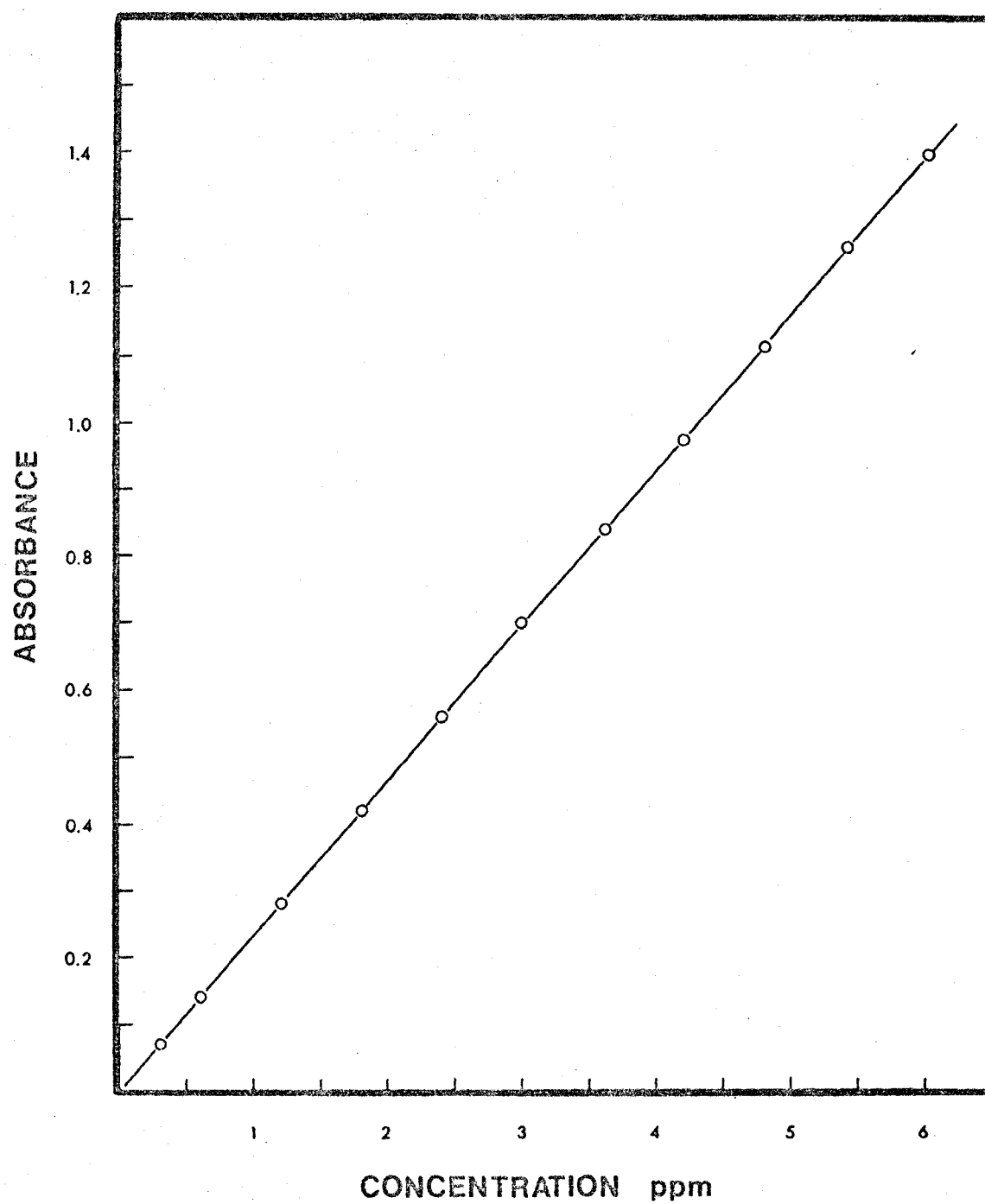


TABLE XI
RINGBOM DATA
FOR IRON (II)

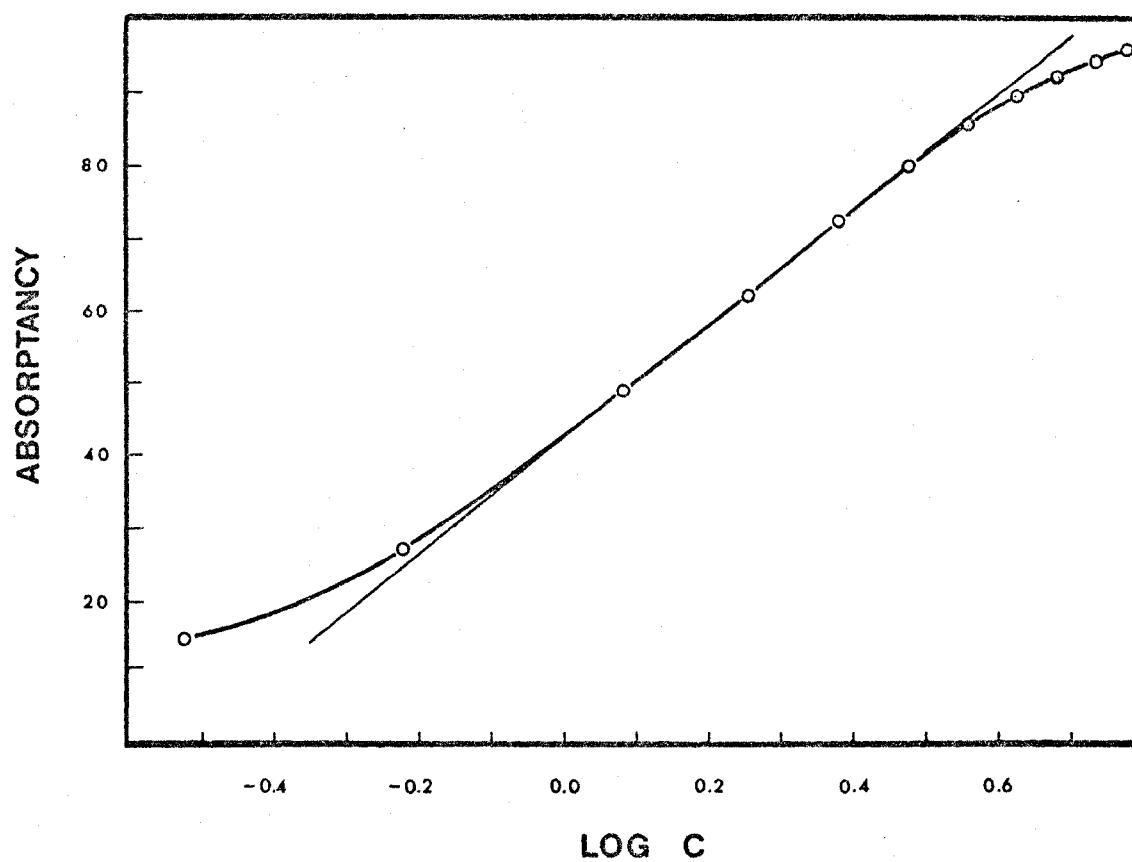
Absorbance A	Transmittance %T	Absorptancy 100-T	Concentration ppm
0.069	85.0	15.0	0.30
0.140	72.6	27.4	0.60
0.281	52.3	47.7	1.20
0.421	37.9	62.1	1.80
0.560	27.7	72.3	2.40
0.700	20.0	80.0	3.00
0.842	14.4	85.6	3.60
0.975	10.6	89.4	4.20
1.114	7.7	96.3	4.80
1.260	5.5	94.5	5.40
1.398	4.0	96.0	6.00

FIGURE 17

RINGBOM PLOT FOR IRON (II)

DETERMINATION

FIGURE 17



obtained from a series of analyses at three points on the Beer's law curve. The results of this study, which indicate excellent accuracy and reproducibility, are presented in Table XII.

11) Effect of Diverse Ions

The effect of diverse ions was studied by adding 5 mg of a diverse ion to a solution containing 120 μ g of iron and performing the recommended procedure. A relative deviation of 2% absorbance was considered tolerable. The following ions did not interfere: Li^+ , Na^+ , K^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , La^{3+} , Ti^{4+} , Hf^{4+} , Nb^{5+} , Mo^{6+} , W^{6+} , Mn^{2+} , Re^{7+} , as ReO_4^- , Re^{3+} , Os^{8+} , Rh^{3+} , Ir^{3+} , Pt^{2+} , Pt^{4+} , Zn^{2+} , Cd^{2+} , Al^{3+} , Ga^{3+} , In^{3+} , Tl^+ , Ce^{3+} , Sn^{4+} , Sn^{2+} , As^{3+} , As^{5+} , Sb^{3+} , Bi^{3+} , F^- , Cl^- , Br^- , I^- , NH_4^+ , OAc^- , NO_3^- , NO_2^- , ClO_4^- , ClO_3^- , SO_4^{2-} , SO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, PO_4^{3-} , and $\text{P}_2\text{O}_7^{4-}$. The above ions did not represent any type of upper limit, and larger amounts could probably be tolerated. Up to 2.0 g of tartrate and a total of 2.0 g of citrate could be tolerated. Up to 200 mg of nitrilotriacetic acid and 100 mg of SCN^- did not interfere. Gold (III) and mercury (II) did not interfere if the solution was filtered prior to reading. Up to 3 mg of Ag^+ could be tolerated if filtered. The following amounts of ions represent the upper tolerable limits: 3 mg of

TABLE XII

STATISTICAL STUDY

RESULTS FOR IRON (II)*

Experiment	Iron taken	ppm found	Relative error %	Standard deviation ppm	Range ppm
1	0.60	0.60	0.00	0.003	0.009
2	2.40	2.40	0.00	0.003	0.013
3	4.20	4.20	0.05	0.012	0.034

*Each result is the average of 11 separate analyses

Zr^{4+} , 2.5 mg of VO_3^- , 4 mg of V^{3+} , 2.5 mg of Cr^{3+} and 3 mg of Pb^{2+} . Up to 500 mg of EDTA or CN^- could be tolerated by the system if added after heating. Palladium (II) did not interfere if CN^- was added after heating. In order to assess the tolerance of the system to copper and nickel, the amounts of these ions were increased until they constituted an interference. Up to 20 mg of Ni^{2+} could be tolerated when 200 mg of NTA were added before the reagent and 200 mg CN^- were added after heating. Above this level, nickel used up too much reagent, and development of the iron complex was incomplete. Up to 50 mg of Cu^{2+} or Cu^+ could be tolerated if 200 mg of CN^- were added after heating. Above this level, the absorbance of the copper complex rose above tolerable limits. Of the ions studied, Ru^{3+} , Co^{2+} and Se^{4+} interfered severely and required prior separation.

D. DISCUSSION

In the present work, 2,2'-dipyridyl- α -glyoxime has been applied to the spectrophotometric determination of iron (II) in an alkaline citrate medium. The procedure has the advantages of speed, simplicity of manipulation, colour stability, high selectivity and good sensitivity.

Iron is one of the most abundant of the metals (65) and is widely distributed in nature. It seldom comes in the natural state, but is found combined with a number of other elements in its ores (66, 67). In waters, biochemically important materials and certain alloys, iron occurs as a trace component (68) with large numbers of other elements. For this reason, a highly selective series of reagents are needed in order to determine this element without a number of time consuming separation steps. As the diverse ion study shows, the reagent is highly selective under the conditions of analysis.

Speed and manipulative simplicity are important in spectrophotometric analysis. The method presented is relatively rapid and very simple to perform. The order of reagent addition is unimportant. The only condition which must be fulfilled is that the reagent should be added before the buffer so that there will be no hydroxide formation which causes low results. There is no extraction

to be performed with its inherent manipulative complexity which could cause low results if incomplete.

The iron (II) complex, furthermore, is quite stable. This is to be expected from a study of other ferroin reagents, since these ligands have sufficiently strong ligand fields to bring about electron pairing in the 3d orbitals of iron (II) (69). This electron pairing also confers kinetic inertness on the resulting complexes as well as high thermodynamic stability. Thus, cyanide can be added to the solution of the complexed iron (II) without effect on absorbance.

E. SUMMARY AND CONCLUSIONS

The spectrophotometric determination of iron (II) presented in this dissertation involved the formation of a highly coloured, red complex between divalent iron and 2,2'-dipyridyl- α -glyoxime in an alkaline citrate medium. Citrate is used in the system to prevent precipitation under the alkaline conditions employed for analysis. The laborious adjustment of pH to between 9.5 and 11.5 is eliminated by the use of an ammonia-ammonium chloride buffer at a pH of 10.5. A 5 minute heating time at a boil is needed for rapid completion of colour development. The absorbance is read at 534 nm against a reagent blank prepared in the same manner.

A large number of parameters were studied. A large excess of reagent was used in order to effect complete development. This excess did not interfere at the analytical wavelength. The system was very stable toward a large number of masking agents allowing high selectivity to be obtained. Of some 72 ions investigated, only three interfered requiring prior separation. The system could tolerate large amounts of copper and nickel, two elements which are frequently found with iron. These two ions also interfere in a majority of the methods for the determination of iron at the trace level (70).

This study has indicated that 2,2'-dipyridyl- α -glyoxime could be used for the trace determination of iron (II) in complex matrices on a rapid, routine basis.

GENERAL SUMMARY AND CONCLUSIONS

The α and β isomers of 2,2'-dipyridyl-glyoxime have been isolated and characterized. The characterization was based on both spectral and chemical data.

A series of spectrophotometric procedures for the determination of microgram quantities of palladium, gold and iron have been developed. These were based on sensitive colour reactions between these metal ions and the α -isomer.

By the proper choice of pH, extraction and masking agents, high selectivity was obtained. The resulting procedures had the advantages of simplicity and rapidity.

Data for the reactions of various other metals with 2,2'-dipyridyl- α -glyoxime is summarized in the Appendix.

APPENDIX

Data for the reactions of various metal ions with 2,2'-dipyridyl- α -glyoxime is summarized below:

Copper (II)

Copper (II) reacted with the reagent over a pH range of 11 to 13 to form a water-soluble green-coloured complex. This complex had a molar absorptivity of 5×10^3 at the wavelength maximum of 430 nm.

Copper (I)

Copper (I) was formed by the reduction of copper (II) with hydroxylamine. Copper (I) reacted with the reagent over a pH range of 11 to 13 to form a green, water-soluble complex, having a molar absorptivity of 9×10^3 at the absorption maximum of 444 nm.

Nickel (II)

Nickel (II) reacted with the α -glyoxime in ammoniacal solution to form a dark red precipitate. The reaction took place over the pH range of 6 to 12.

Cobalt (II)

Cobalt (II) reacted with the reagent to give a bright

yellow precipitate over a pH range of 8 to 12. This complex was not decomposed by either acid or cyanide.

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